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AN INTRODUCTION TO SURFACE CHEMISTRY

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AN INTRODUCTION TO SURFACE CHEMISTRY

By

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HUMPHREY OWEN JONES LECTURER IN PHYSICAL CHEMISTRY
CAMBRIDGE UNIVERSITY

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1930

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Wilt Thou not ope the heart to know
What rainbows teach and sunsets show?
EMERSON.

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PREFACE TO THE FIRST EDITION

By Professor F. G. DONNAN

THE importance of an accurate study of the actions, equilibria, and structures which occur at the interfaces between homogeneous phases of matter is widely recognised at the present time. Thus a knowledge of these matters is required for a proper understanding of adsorption, the formation and stability of disperse or micro-heterogeneous systems (colloid sols and gels), catalysis, enzyme actions, etc., whilst the progress of research shows more and more clearly that the phenomena of life, i.e. the behaviour of cells and tissues, are intimately concerned with the actions occurring at surfaces, and that the effects produced by drugs, disinfectants, and other substances which profoundly affect the operation of cells and micro-organisms are largely due to surface actions.

From the general statistical and thermodynamic point of view, the scientific theory of surface phenomena was placed on a satisfactory basis by the researches of J. Willard Gibbs, Sir J. J. Thomson, and J. D. van der Waals. In comparatively recent times the more intimate molecular study of the structures and kinetics of surfaces has advanced very rapidly, thanks more especially to the pioneer work of Lord Rayleigh, André Marcelin, Sir W. B. Hardy and Irving Langmuir. Our knowledge of this subject has been greatly increased during the last few years by the excellent work of N. Adam and of E. K. Rideal. The combined effect of these researches has been to reveal the existence of a newly recognised so-called "two dimensional" molecular world, the dynamics of which is analogous to that of the ordinary "three dimensional" molecular world of homogeneous phases in bulk, whilst the structure of this "surface world" presents new phenomena of molecular orientation of the highest importance for the understanding of great regions of natural phenomena. The great merit of Dr E. K. Rideal's book lies in the fact that the author, whilst in no wise neglecting the thermodynamic treatment and its results, gives a very admirable account of this more recent and extremely important field of study. Since this is also the most promising line of advance in the investigation of disperse systems, Dr Rideal's book can be most warmly recommended to all who are interested in colloid physics and chemistry. In the last two chapters the author gives a good introduction to the principal facts and theories of what is usually understood to-day as colloid chemistry, so that the reader is fully supplied with everything that is necessary for a thorough understanding of this subject. Every student and investigator of surface and colloid phenomena owes Dr Rideal a warm debt of gratitude for his admirable survey and presentation of a great and rapidly advancing field of physico-chemical science.

F. G. D.

UNIVERSITY COLLEGE,
LONDON.

April, 1926.

INTRODUCTION TO THE FIRST EDITION

THE essential differences between the properties of matter when in bulk and in the colloidal state were first described by Thomas Graham. The study of colloid chemistry involves a consideration of the form and behaviour of a new phase, the interfacial phase, possessing unique properties. In many systems reactions both physical and chemical are observed which may be attributed to both bulk and interfacial phases. Thus for a proper understanding of colloidal behaviour a knowledge of the properties of surfaces and reactions at interfaces is evidently desirable.

Whilst the conditions of equilibrium for such systems were clearly enunciated by J. Willard Gibbs and Sir J. J. Thomson a great impetus was given to the subject by supplementing the formal thermodynamic treatment with a clearer visualisation of the molecular structure of surfaces by Sir W. B. Hardy and I. Langmuir.

In this monograph an attempt has been made to present the subject from this point of view, and whilst the text is admittedly incomplete as a compendium on colloid chemistry yet it is hoped that the elaboration of the physics and chemistry of these degraded two-dimensional systems may prove of value to those concerned in problems of colloidal behaviour.

I wish to thank Professor F. G. Donnan for his stimulating interest, and to express my gratitude for the great assistance given me by Mr M. T. Sampson, Mr R. K. Schofield and Mr A. P. Cary who have been engaged in investigations on the properties of surfaces in this laboratory. But for their interest and labour this book would never have been planned and written.

ERIC K. RIDEAL

LABORATORY OF PHYSICAL CHEMISTRY,
CAMBRIDGE.

April, 1926.

INTRODUCTION TO THE SECOND EDITION

THE rapid growth in both the scientific study as well as in industrial applications of the chemistry and physics of colloidal systems during the last few years is clearly marked both in the vigorous activity of special societies devoted to these ends as well as in the marked increase in the number of publications on such subjects. As a preliminary to such investigations an adequate understanding of the properties of the simpler systems such as surfaces and interfaces has become not less but rather more important as the complexity of the subject increases. We may likewise note that in certain fields the properties of surfaces and membranes rather than those of disperse systems seem to be acquiring positions of increasing importance; to cite only two instances from amongst many of diverse character may be mentioned the study of thermionics, revealing new properties of films at solid gas interfaces, and the increasing importance attached by investigators to the functions and properties attributable to membranes and interfaces in biology.

In this second edition an attempt has been made to revise and review our present knowledge of the properties of interfacial phases but as in the first edition, to keep the volume within reasonable dimensions, the general properties of disperse systems have not been elaborated in any detail.

I wish to express my gratitude for the assistance given to me by many, especially by Mr N. A. de Bruyne, F. P. Bowden, W. L. Francis and C. G. Lyons, who have been engaged in investigations on the properties of surfaces in this laboratory.

E. K. R.

January 1930.

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CHAPTER I

THE SURFACE TENSION OF LIQUIDS

1. The existence of surface phases.

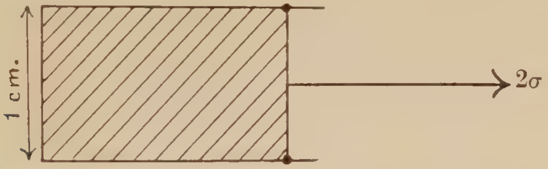
It has been found that where one distinct phase adjoins another there exist conditions which distinguish the behaviour of a thin layer of matter at the boundary from that of the general mass in either of the homogeneous phases which bound it. Under certain circumstances at least, and perhaps always, the boundary is not simply a geometrical surface upon one side of which there is one phase of uniform properties and on the other a second phase, everywhere distinct from the first and homogeneous in itself: nor, again, do the contiguous phases shade, as might equally well be supposed, rapidly but continuously one into the other, so that the boundary would have to be considered as a more or less arbitrary mathematical definition rather than a physical entity: it lies in a film or lamina of finite though minute thickness consisting of an entirely new phase of definite and measurable properties. To this phase our attention will be given in the following pages. It will be seen that two of its dimensions may be varied at will, like those of a phase in bulk, while its third dimension, which lies at right angles to the plane of the lamina, is fixed: if in any way it be altered, a new superficial phase is formed.

A number of different types of such interfacial phases must be considered when dealing with bulk phases in their different physical states. Of special importance are the interfaces formed by contact of a bulk liquid with gaseous, liquid and solid phases whilst the problems connected with heterogeneous catalysis necessitate an examination of the properties of the solid-gas interface.

The mathematical treatment of surfaces was developed much earlier than the direct examination of superficial films. It is based primarily upon the observed tendency of a volume of liquid to adopt when unconstrained a shape with a minimum surface. The property of having a minimum surface for a given volume is possessed by a sphere, and this shape is assumed by a free body of liquid. A falling raindrop is spherical: upon this fact indeed is based the theory of the rainbow. In Plateau's beautiful experiment a drop of oil is formed in an aqueous solution of the same density by means of a tube dipping below the surface. The drop grows to any desired size, and when detached from the tube and floating without influence of gravity it assumes a spherical shape. If distorted it will vibrate about its spherical figure of equilibrium. Upon any sufficiently small drop the influence of gravity, which increases with the cube of the radius, becomes negligible in comparison with the surface forces which depend on the square of the linear dimensions, so that dew-drops on spiders' webs or beads of liquid on the leaves of plants are almost spherical. If the surface is partly constrained it will adopt the least superficial area consistent with the constraint. This fact may be well illustrated by stretching a soap-film on a wire frame-work. A loop of cotton may be laid on the film, which is then broken within the loop; the outer part of the film drags out the cotton until its shape is circular and the film area has thereby become a minimum. By using several cotton threads knotted together we may vary this experiment as we please, always obtaining a figure of minimum surfaces. This fact has been applied practically to the design of structures.

A liquid thus behaves rather as if it were surrounded by an elastic skin with a tendency to contract. In a soap-film the force of contraction may be measured directly by suspending from a balance-pan a light square framework hanging in a vertical plane so that the lower horizontal bar is immersed in a soap solution and the part between the surface and the upper bar is covered with a film. The film tends to contract and to pull down the balance-pan. The pull is proportional to the horizontal length of the film: it is found under ordinary conditions to be about 23 dynes/cm. for each side of the film. The quantity thus measured is named the surface tension and may be defined as the force exerted on a straight line of unit length in the surface, in a direction parallel to the surface but perpendicular to the line. Imagining the length of the line and its proportional tension to diminish indefinitely, we arrive in the limit to the conception of surface tension at a point on the surface. The quantity, surface tension, will be denoted by the symbol σ. The usual unit is one dyne per cm.: in older works however one mgm. weight per mm. is used, a unit 9·81 times as great.

There is another point of view from which it is often useful to regard surface phenomena. If the surface of a soap-film in a wire frame is increased by moving outwards against the tension one side of the frame, a quantity of work must be done against the surface tension equal to the product of the surface tension and the increase of area. A definite quantity of potential energy is thus bound up with each unit of surface. The numerical value of the surface energy defined as energy per unit surface is clearly the same as that of the surface tension. The dimensions in each case are $\frac{[\text{Mass}]}{[\text{Time}]^2}$. Since the potential energy of the system tends to a minimum, the surface must contract to a minimum area: we are thus led to the same result as before.



It is important to observe that the surface energy σ is a quantity of the kind called "free energy" by Gibbs and Helmholtz. It does not represent the whole of the energy expended when a fresh surface is formed. If the extension of surface takes place adiabatically, a quantity of heat $-T\frac{d\sigma}{dT}$ is absorbed from the interior, which is thereby somewhat cooled. Allowing for the additional energy, which may be called the latent heat of surface formation, introduced to compensate for this cooling effect, the total energy per unit of fresh surface is $\sigma - T\frac{d\sigma}{dT}$: this quantity is known as the *Total Surface Energy*: (u). We are as a rule more concerned with the free surface energy, and the latter quantity will be understood when for shortness the term "surface energy" is used.

2. The surface energy of liquids.

In the previous section we have noted that in the formation of an interfacial phase energy must be expended and that the free surface energy of an interface is related to the total surface energy by the Gibbs-Helmholtz equation

$$\sigma - u = T \frac{d\sigma}{dT};$$

thus the total interfacial energy may be determined from measurements of the free surface energy and the temperature coefficient of this quantity. Whilst computation of the surface energy for interfaces between solids and liquids or gases is a difficult matter, in the case where both the bulk phases are mobile, such as at liquid-gas or liquid-liquid interfaces, the value of the interfacial surface tension or free surface energy is readily determined.

The methods of measurement of the surface energy of liquids may be divided into two classes, the static and dynamic methods. In general, for pure unassociated liquids in contact with their vapour alone, the values of the surface energy determined by the two methods do not differ beyond the range which may be attributed to experimental error. In other cases, however, marked divergence between the values obtained by the two methods is to be noted. This divergence is, as we shall have occasion to note, due to the comparatively slow rate of attainment by diffusion of equilibrium in the surface phase of solutions.

The static methods include the following:

(1) The rise or fall of liquid in a capillary tube or between plates inclined at a small angle.

(2) The weight of drops falling from a circular tube.

(3) The maximum pressure within a bubble of gas in the liquid.

(4) The measurement of the dimensions of curved liquid surfaces or bubbles.

(5) The direct pull of a soap-film or ring from off the surface of a liquid.

(6) Langmuir's differential method for thin insoluble films on liquid surfaces.

Whilst the dynamic methods include

(7) The ripple method.

(8) Vibrating jets of fluid.

(9) Vibrating drops.

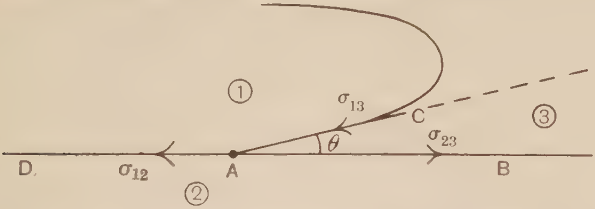
(10) Rate of flow of liquids in capillary tubes.

These methods are capable both of endless variations to suit any particular set of circumstances and of numerous modifications limited only by the ingenuity of the experimenter.

3. The angle of contact.

Whilst certain of these methods involve measurements only at the liquid-vapour or liquid-liquid interfaces involved, in the static methods we must usually consider, besides the interfacial energy of the two fluids, that between each of them and a solid.

There is at present no means of measuring satisfactorily the energy at any solid surface, but the two energies of this kind may be eliminated from the calculation by taking into consideration the "angle of contact" in the following manner.



Let (1) and (3) represent two fluids in equilibrium on a solid (2), AD, AB the two solid-fluid and AC the fluid-fluid interface, the line AC forming an angle θ with AB. This angle is called the angle of contact of the system. Then, since AC represents the equilibrium configuration of the system, we obtain

$$\sigma_{12} + \sigma_{13} \cos \theta = \sigma_{23} \quad \text{.....................(1)},$$

where σ_{12} represents the interfacial tension between the solid (2) and the first fluid (1), σ_{13} the fluid-fluid interfacial tension, and σ_{23} the interfacial tension between the second fluid and the solid. This expression was first obtained by Neumann.

If we denote by W the work required to separate the first fluid from the solid perpendicularly to the plane of contact, then

$$W = \sigma_{23} + \sigma_{13} - \sigma_{12} \quad \text{.....................(2)},$$

a relationship known as the equation of Dupré.

From (1) and (2) we obtain the relationship due to Young:

$$W = \sigma_{13}(1 + \cos\theta) \quad \text{.....................(3)}.$$

If there be no adhesion $\cos\theta$ becomes zero, whence $W = \sigma_{13}$, whilst, as the adhesion of the liquid for the solid increases, the angle of contact diminishes until the point is reached where the work of adhesion of the liquid to the solid is equal to the cohesion of the liquid, or $W = 2\sigma_{13}$, and the angle of contact vanishes.

It is found that in a number of cases a solid surface can be prepared so that a liquid will wet it and will slide freely over the surface: under these conditions the angle of contact is actually zero (Volkmann, *Ann. der Physik*, LIII. 633, 1894; Carver and Hovorka, *Journ. Inst. Metals*, 1325, 1925). For determination of contact angles it is convenient to use surface tension measurements by two methods, of which one depends upon, and the other is independent of, the angle of contact. Such a pair of methods are the capillary rise and the bubble pressure methods. If the surface tensions as calculated by these two methods agree to within one part in 500, it may be concluded that $\sin\theta < \frac{1}{500}$ or $\theta < 7'$ of arc. This is true of most pure wetting liquids for which accurate values of σ by two such methods are available. By various direct measurement methods Magie (*Phil. Mag.* XXVI. 150, 1888), Langmuir (*Trans. Farad. Soc.* XV. 62, 1920), Anderson and Bowen (*Phil. Mag.* XXXI. 143, 285, 1916) and Richards and Carver (*J.A.C.S.* XLIII. 827, 1921) have likewise concluded that the angle of contact is zero under these conditions.

A contact angle of zero or 180° implies that the liquid or gaseous surface is asymptotic to the solid at contact. In a capillary tube a liquid with zero angle of contact must therefore wet the tube to some distance above the visible meniscus. It is an experimental fact that, unless care be taken to observe this condition, erratic values for σ are obtained, no doubt because then the angle of contact does not vanish. A liquid with an angle of contact of 180° should similarly fail to wet a containing tube until well below the meniscus: the column of liquid will then be shielded by a gas film from the glass tube until this film is squeezed out by the hydrostatic pressure of the column. A zero contact angle between a given liquid and solid is equivalent therefore to the spreading of the liquid over the solid in presence of the gaseous phase present.

The true value of the angle of contact for fluids which do not wet surfaces in such a manner that the fluid can slide freely over the surface is not readily determined, for there are numerous sources of constraints which appear similar in kind to frictional resistance, precluding the possibility of arriving at the true position of equilibrium. Thus Quincke found that the angle of contact of mercury-air on a glass plate was initially 148° 55′, but this value fell after two days to 137° 14′. We shall have occasion to revert to the problem of the determination of the angle of contact for non-wetting fluids in discussion on the methods of determination of the surface tension and in dealing with the properties of membranes.

In the following pages a brief description of the more important methods employed for the accurate determination of the surface tensions of liquids is given, whilst a very complete account can be found in *Bull.* No. 540, U.S. Bureau of Standards, compiled by N. E. Dorsey.

4. The capillary rise method.

Of the methods of measuring surface tension, that depending on the rise of a liquid in a capillary tube has been more widely used than any, with the possible exception of the drop-weight method. This is because, of all the static methods, of methods, that is, which give an equilibrium value for the surface tension, the conditions are the most clearly defined, and the calculations based upon them have a greater degree of certainty. It can be used equally at high and at very low temperatures: by this means Ramsay carried out determinations of the surface tension of organic liquids up to their critical points, and Kamerlingh Onnes that of hydrogen almost to its freezing point.

When a glass capillary tube is dipped into water, the liquid rises in the tube above the general level of the water to a height which is approximately in inverse proportion to the radius of the tube. We may explain this event somewhat as follows: Water wets glass; it tends, that is, to spread over its surface and displace therefrom the air. In order that this may occur the sum of the surface energies involved must be reduced, and if nothing hinders (that is if the contact angle be zero), the water will continue to spread until all the glass is covered or all the water has been used to form a thin continuous film. When a vertical tube provides the surface over which the water must spread, we have however a balancing tendency due to the effect of gravity on the water raised up in the tube. If the tube is narrow enough, the rise of level is easy to calculate from the principle of virtual work. Let σ_1, σ_2, $\sigma_{1\cdot 2}$ represent the surface tension of water-air, glass-air and glass-water respectively. Imagine an infinitesimal rise of the liquid in the tube above its equilibrium position, without change of shape of the meniscus and therefore without altering the total free surface energy water-air. If h be the equilibrium height of the liquid, δh the increase to this and r the radius of the tube, the surface glass-air will be diminished and the surface glass-water increased by an amount $2\pi r\,\delta h$ cm.^{2} The surface energy will thus be diminished by $(\sigma_2 - \sigma_{1\cdot 2})\,2\pi r\,\delta h$. The potential energy due to gravity will at the same time be increased by $g\pi r^2 h\,(\rho_l - \rho_g)\,\delta h$, where ρ_l, ρ_g are the densities of water and air respectively. Since the resultant energy change must be zero, we have

$$(\sigma_2 - \sigma_{1\cdot 2})\,2\pi r\,\delta h = g\pi r^2 h\,(\rho_l - \rho_g)\,\delta h,$$

$$\therefore\ h = \frac{2\,(\sigma_2 - \sigma_{1\cdot 2})}{gr\,(\rho_l - \rho_g)}.$$

Now $\sigma_2 - \sigma_{1\cdot 2} = \sigma_1 \cos\theta$, where θ is the angle of contact,

$$\therefore\ h = \frac{2\sigma_1 \cos\theta}{gr\,(\rho_l - \rho_g)}.$$

If the tube is not infinitesimal in radius, the calculation becomes more difficult, because we shall have to consider not only the form of the meniscus (in order to calculate its volume) but also the direction in which that form tends to change under the disturbance imagined. The general problem has been solved by Rayleigh (*Proc. Roy. Soc.* A, XCII. 184, 1915) and by Verschaffelt (*K. Akad. Amsterdam Proc.* XXI. 366, 1919) for sufficiently small tubes, with the result that if θ denotes the angle of contact of the liquid with the wall of the capillary tube, then

$$\frac{2\sigma\cos\theta}{g(\rho_l-\rho_g)} = r\left[h + \frac{r}{3}\sec^3\theta\,(1-\sin\theta)^2\,(1+2\sin\theta) + \frac{1}{3}\frac{r^2}{h}\sec^2\theta \right.$$

$$\left. \times\left\{\sec^4\theta\,(1-\sin\theta)^3\,(1+\sin\theta+2\sin^2\theta) + 2\log\frac{1+\sin\theta}{2}\right\}\right],$$

or, if the angle of contact be zero,

$$\frac{2\sigma}{g(\rho_l-\rho_g)} = r\left\{h + \frac{r}{3} - 0{\cdot}1288\frac{r^2}{h} + 0{\cdot}1312\frac{r^3}{h^2}\right\}.$$

The first expression holds, provided that the cube of r/h is negligible in comparison with unity, and the second if the fourth power of r/h is negligible.

For very large tubes Rayleigh finds

$$\frac{r\sqrt{2}}{a} - ln\,\frac{a}{h\sqrt{2}} = 0{\cdot}8381 + 0{\cdot}2798\,\frac{a}{r\sqrt{2}} + \frac{1}{2}\,ln\,\frac{r\sqrt{2}}{a},$$

where $a^2 = \dfrac{2\sigma\cos\theta}{g(\rho_l-\rho_g)}$. This formula is accurate enough for any practical purpose if $\dfrac{r\sqrt{2}}{a} > 6$.

For intermediate values of r/a, or for tubes of intermediate size, no general formula has been given. Bashforth and Adams have however published tables from which the form of any capillary surface may be calculated, and with the aid of these Sugden has further calculated a table of values of r/b for all values of r/a between 0 and 6. b is here the radius of curvature at the crown of the meniscus, and, since $h = \dfrac{2\sigma_1\cos\theta}{g(\rho_l-\rho_g)\,b}$ accurately, the capillary rise for a tube of any diameter may be calculated (Sugden, *J.C.S.* CXIX. 1483, 1921; Bosanquet, *Phil. Mag.* VII. 296, 1928). This table is reproduced in part on p. 10.

The capillary rise h, which has been discussed hitherto, is of course the height of the capillary meniscus above that of an unbounded expanse of liquid, whose level is therefore unaffected by surface tension. In practice it is not usually convenient to employ so large a quantity of liquid as is demanded by this condition, but instead two interconnected tubes, one of capillary and one of wide bore, are filled with liquid. The height h between the two liquid levels is now the difference between two quantities h_1 and h_2 defined by

$$h_1 = \frac{2\sigma \cos\theta}{g(\rho_l - \rho_g)\, b_1},$$

and
$$h_2 = \frac{2\sigma \cos\theta}{g(\rho_l - \rho_g)\, b_2},$$

whence
$$h = h_1 - h_2 = \frac{2\sigma \cos\theta}{g(\rho_l - \rho_g)} \left(\frac{1}{b_1} - \frac{1}{b_2}\right).$$

$\frac{r}{a}$	$\frac{r}{b}$	$\frac{r}{a}$	$\frac{r}{b}$
0	1	0	1
0·1	·9968	0·9	·7875
0·2	·9869	1·0	·7490
0·3	·9710	1·5	·5545
0·4	·9498	2·0	·384
0·5	·9236	3	·149
0·6	·8936	4	·056
0·7	·8606	5	·020
0·8	·8249	6	·006

To obtain reliable results it is essential in the first place to ensure purity of the liquid and absolute cleanliness of the apparatus, especially from oily or greasy matter. The latter can most readily be removed by treating the apparatus, after preliminary cleansing, with warm aqua regia or chromic acid, and finally steaming for about half an hour. The apparatus should therefore be designed to facilitate this thorough cleaning. These conditions of course apply equally to any method of measuring surface tensions.

The diameter of the capillary tube must be known with accuracy and the cross-section must be truly circular. It is not as a rule easy to obtain tubing of uniform circular bore*, but in default of time for the tedious process of calibrating tubing the difficulty may be overcome by the following method due to Ferguson (*Proc. Phys. Soc.* XXXVI. 37, 1923): Lengths of capillary tube are examined under a micrometer until one is found whose end cross-section is circular. This tube is then used so that the measured end dips downwards into the liquid; the upper end, instead of being open to the atmosphere, is connected to a source of pressure and a manometer, and the meniscus is forced down until its lowest point is level with the end of the tube, so as to be observed at the only point where its curvature is accurately known. If then p be the pressure in dynes/cm.² recorded by the manometer, we have

---

* Harkins tested several hundreds of feet of tubing before finding a length suitable for this purpose.

$$2\sigma \cos\theta \left(\frac{1}{b_1} - \frac{1}{b_2}\right) = gh\,(\rho_l - \rho_g) + p.$$

The first term may now be negative.

In Ramsay's experiments the forms of apparatus used were capable of sustaining pressures up to 100 atmospheres. The wide and narrow tubes were concentric: the wide tube was therefore annular in shape, and the allowance for the capillary rise in it becomes difficult to calculate. Ramsay did not make a sufficient allowance for the rise in the annular tube and in consequence all his values, and those of later workers who have adopted his figures for purposes of calibration for surface tensions, are too low. Sugden has used an approximate method of correcting for the rise in the annulus, in which he considers a capillary tube of circular bore which gives an identical rise at a particular temperature and for a particular liquid, and assumes that the rise in the two tubes will be the same for all other temperatures and liquids. By this means he has, with the help of later measurements, corrected all Ramsay's values for which sufficient data are given in the original papers.

Modifications of the method.

Instead of a capillary dipping into a large vessel of liquid, we may reduce the quantity of fluid needed and simplify the measurement of the height h by using a U-tube of which one branch is of capillary and the other of wider bore. The difference h of height between the liquid in the two branches can then be easily read by means of a cathetometer or found by a slight modification of Ferguson's method.

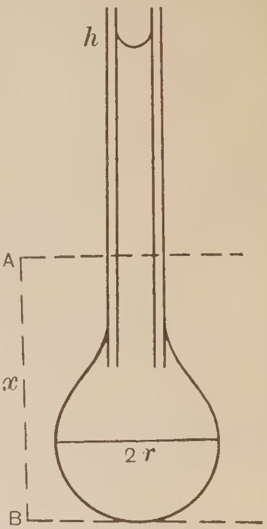
Again, the case of two parallel plates dipping vertically or inclined at a slight angle at a short distance apart in the liquid closely resembles that of the capillary tube and has been used by Quincke and Volkmann.

For the case of the parallel plates the equation for the surface tension is approximately

$$\sigma = \frac{dhg\,(\rho_l - \rho_g)}{2},$$

where d is the distance between the plates. This method compares unfavourably with the preceding ones, owing to greater difficulties of adjustment, the necessity for using optically plane glass, and larger quantities of liquid.

In the determination of the surface tension of a liquid by means of the capillary tubes a knowledge of the angle of contact is necessary. Sentis (*Journ. de Phys.* 2. VI. 571, 1887; *ibid.* 3. VI. 183, 1897) has modified the capillary tube method in such a way as to eliminate the necessity for this observation. The liquid is introduced into a vertical capillary tube until a drop is formed at the lower end of maximum diameter $2r$; the drop is supported by the surface forces and the liquid column in the tube is at a point h. A free surface of the liquid is now brought up from underneath until it just touches the drop at B and the column in the capillary tube falls. The free surface is now raised to A until the liquid in the tube rises to its original position h. If the distance the liquid is raised from B to A be x, then



$$\frac{2\sigma}{(\rho_l - \rho_g)\,g} = r\left[x + \frac{r}{3} - 0{\cdot}1288\,\frac{r^2}{x} + 0{\cdot}1312\left(\frac{r^3}{x^2}\right)\right].$$

5. The drop weight method.

The method of measuring the surface tension of a liquid from the weight of a drop formed slowly and allowed to drop from a tip ground plane and with a sharp circular edge, has frequently been employed owing to the simplicity of the method.

The experimental difficulties to be overcome in order to obtain reproducible results consist in great measure of ensuring that the drop shall be allowed to form on the tip, which the liquid must wet uniformly, so slowly that it is practically in static equilibrium at the moment before it is detached. Loss by evaporation from the receiving vessel may thus be an important factor for which correction must be applied. Again, for many solutions the rate at which the gas-liquid interface attains equilibrium is extremely slow; this is especially true for many solutions of biological importance which contain materials of low diffusivity. Thus it may be necessary to permit a drop to hang under conditions approaching its maximum size for several minutes to ensure the attainment of such equilibrium.

Tate (*Phil. Mag.* XXVII. 176, 1864) discovered empirically that the weight of a drop of liquid falling from the end of a tube was proportional to the radius of the tube and the surface tension of the liquid.

The theoretical formula for the maximum weight of a cylindrical drop hanging from a tube in equilibrium was shown to be

$$W = 2\pi r\sigma - \pi r^2\sigma\left(\frac{1}{r}\right) = \pi r\sigma$$

by Worthington (*Proc. Roy. Soc.* XXXII. 362, 1881; *Phil. Mag.* 1884, 1885) and Rayleigh (*Phil. Mag.* XLVIII. 321, 1899).

Rayleigh showed, however, that in practice this equation required modification, and found for tubes of moderate radius that a better agreement was obtained by the relationship

$$W = 3{\cdot}8 r\sigma.$$

For very small or very large tubes, however, the value of the "constant" 3·8 rises well above 4.

Morgan and his co-workers (*J.A.C.S.* 1908–1913) have published a number of papers in support of "Tate's laws," claiming that under suitable conditions $W = Kr\sigma$, where K is a constant. This view, however, cannot be substantiated.

This variation is of course due to the fact that the actual detachment of the drop is an extremely complicated dynamical process (cf. Perrot, *J. Chim. Phys.* XV. 164, 1917), and that during the growth and detachment of the drop the sides of the cylinder of emerging liquid commence to curve; at the moment of detachment, as Freud and Harkins point out (*J.P.C.* XXXIII. 1224, 1929), the correct equation for the weight of the drop should be

$$W = 2\pi r\sigma - \pi r^2\sigma\left(\frac{1}{r} + \frac{1}{s}\right),$$

where s is this second curvature.

Visual observation indicates that the curvature of s has the opposite sign from r and is numerically almost equal to it. If these conditions were strictly valid during the process of detachment, we should obtain

$$W = 2\pi r\sigma$$

for the weight of the ideal drop.

In practice the changing contour of the drop with its size renders the determination of the curvature of the drop at the point of contact with the tip a difficult matter, and in actual practice an empyric factor has been introduced by Löhnstein (*Zeit. Physikal. Chem.* LXIV. 686, 1908). This factor is dependent on the radius of the tip, and the nature of the liquid under investigation. The Löhnstein correction in its final form is accordingly

$$W = 2\pi r\sigma f\frac{r}{a}, \text{ where } a^2 = \frac{2\sigma}{g\rho}.$$

This function is found to be approximately a cubic function of $\frac{r}{a}$, being unity when $\frac{r}{a}$ approaches 0, falling to a minimum of about 0·6 when $\frac{r}{a} = 1{\cdot}1$ and rising thereafter continuously. Harkins and Brown (*J.A.C.S.* XLI. 499, 1919) have made an extensive series of accurate determinations of the Löhnstein correction for tips of various radius, and the various theories as to the theoretical significance of the correction term have been noted by Freud and Harkins (*loc. cit.*), and by Palitzsch. (*Zeit. physikal. Chem.* CXXXVIII. 399, 1928).

Iredale (*Phil. Mag.* XLV. 1088, 1923) has made use of an expression based on the fact that different liquids may form drops of similar shape from tubes of different diameters. From this and from the assumption that rupture occurs at the point of maximum concavity, the equation

$$K^2 = \frac{\sigma_1\rho_2}{\sigma_2\rho_1}$$

is developed, where σ_1, σ_2 and ρ_1, ρ_2 are the surface tensions and densities respectively of two liquids and K is the ratio of the radii of the tubes from which symmetrical drops hang. All that is required for the practical determination of surface tension from this formula "is a knowledge of the tube radius and drop radius ratio, with a continuously varying radius of tube, for some standard liquid of known surface tension and density" (Iredale, *loc. cit.*).

From the data of Harkins (*loc. cit.*) on the drop weights of water from tubes of varying radius we obtain the following data for the radius of drops of water formed at tips of various sizes:

Tube radius r in cms.	Drop radius r' for water	$\frac{r}{r'}$
·09946	·1998	·4977
·14769	·2238	·6603
·19666	·2425	·8112
·23790	·2555	·9863
·27605	·2669	1·035
·29694	·2727	1·088
·32362	·2797	1·157
·37964	·2938	1·289
·44755	·3103	1·442
·55009	·3351	1·643
·65031	·3581	1·816
·72229	·3744	1·929
·77329	·3829	2·019
·84892	·3888	2·184
1·0028	·3900	2·571

With the aid of this table and the equation of symmetry we are in a position to calculate the surface tensions of other liquids from a knowledge of the drop weight and the tip radius alone. The following example given by Iredale may be cited.

The weight of a mercury drop detached from a capillary tube of radius 0·0852 cm. was found to be 0·1794 gm. Since $\rho = 13{\cdot}53$ for mercury, the radius of the mercury drop is 0·1469 cm. Hence

$$\frac{r}{r'} = \frac{0{\cdot}0852}{0{\cdot}1469} = 0{\cdot}5801.$$

From a graph constructed from the table above we find that the tube radius required to give a drop of water of the same characteristic ratio $\frac{r}{r'}$, would be 0·1239 cm. Hence

$$K = \frac{0{\cdot}0852}{0{\cdot}1239},$$

also $\sigma_{H_2O} = 72{\cdot}80$ and $\rho_{H_2O} = 0{\cdot}998$; whence

$$\sigma_{Hg} = \frac{K^2 \rho_{Hg}\, \sigma_{H_2O}}{\rho_{H_2O}} = 466 \text{ dynes per cm.}$$

Many modifications of the drop weight method have been utilised in practice.

Instead of measuring the weight directly we may calculate it from the volume and the density: the drop volume method has been applied by Harkins chiefly to the measurement of the tension between two liquid phases, and it probably falls little short in accuracy from the previous method. More frequently it has been modified, especially for biochemical purposes, as a drop number method: that is, a known volume of liquid is allowed to flow out of a tube, and the number of drops formed is compared with that formed by a standard fluid. This method is necessarily very rough.

Bubble pressure.

By reversing the position of liquid and gas assumed in the preceding section we obtain the bubble pressure method. The theory corresponds closely with that of the drop weight and has been developed by Cantor, Feustel and Schrödinger (*Ann. d. Physik*, XLVI. 413, 1915).

The equation derived is

$$\sigma = \frac{1}{2} r\rho \left(1 - \frac{2}{3}\frac{r\rho}{p} - \frac{1}{6}\frac{r^2\rho^2}{p^2}\right),$$

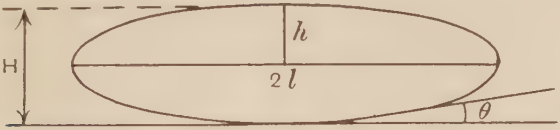
where p is the maximum pressure, and r is now the internal radius of the tube.

The experimental method has been most carefully worked out by Jäger (*K. Akad. Amsterdam Proc.* XVII. 521, 1914), in researches extending over a very wide temperature range. The liquid under investigation is contained in a long narrow bulb through which a tube of glass or platinum is sealed at the top and dips into the liquid, while a second tube is sealed on at right angles near the top. The upper tube is connected to a reservoir of pure nitrogen and to one arm of a manometer whose other arm is in connection with the tube. This method of course gives the surface tension of the liquid against nitrogen saturated with its vapour: and probably differs little as we shall see (pp. 76–77) from that against the pure vapour. Brown (*Phil. Mag.* XXXIX. 1049, 1928) has found this method the most reliable for the determination of the surface tension of mercury.

This method undoubtedly has the widest application of any yet employed, and is at the same time accurate. Among other workers who have used it are Cantor (*Wied. Ann.* XLVII. 399, 1892), Forch (*Ann. Phys. u. Chem.* LXVIII. 801, 1899), Jäger (*Zeit. f. anorg. u. allgem. Chemie*, CI. 1, 1917), Linebarger (*J.A.C.S.* XXII. 5, 1900), Whatmough (*Zeit. physikal. Chem.* XXXIX. 129, 1902), and Somerwald and Drath (*Zeit. anorg. Chem.* CLIV. 79, 1926). Sugden (*J.C.S.* CXXI. 858, 1922) has also extended the method for wide tubes by computing a correction table based upon the data of Bashforth and Adams.

The Method of the Sessile Drop.

In this method either the form of a drop of liquid resting upon a horizontal surface or of a bubble of gas formed under such a surface is studied.



The conditions of equilibrium have been investigated by Quincke (*Ann. d. Phys.* CV. 38, 1858), Magie (*Phil. Mag.* XXVI. 162, 1888), Ferguson (*Phil. Mag.* XXV. 507, 1913), and Verschaffelt (*Koninkl. Akad. Amsterdam Proc.* XXI. 836, 1919). The surface tension of the drop forming liquid is related to the form of the drop by means of the equation

$$\frac{2\sigma}{(\rho_l-\rho_g)\,g}=h^2\left[1-\frac{1{\cdot}724}{lh^2}\left(\frac{\sigma}{(\rho_l-\rho_g)\,g}\right)^{\frac{3}{2}}+\frac{4}{R_0 h}\left(\frac{\sigma}{(\rho_l-\rho_g)\,g}\right)\right]\ldots(1),$$

where h is the distance from the vertex to the plane of maximum horizontal diameter equal to $2l$ and R_0 is the radius of curvature at the vertex of the drop of bubble and is approximately equal to

$$R_0 = \frac{\left(\dfrac{\sigma}{(\rho_l - \rho_g)\,g}\right)^{\frac{3}{4}}}{1{\cdot}16\sqrt{l}}\, e^{\frac{l}{\sqrt{\sigma/(\rho_l-\rho_g)\,g}}}.$$

In general the term containing R_0 is extremely small and can be neglected.

If the surface tension be expressed in terms of the angle of contact, we obtain

$$\left(\frac{\sigma}{(\rho_l - \rho_g)g}\right)^{\frac{1}{2}} = \frac{H}{2\cos\frac{\theta}{2}}\left[1 - \frac{\dfrac{2\sigma}{(\rho_l - \rho_g)g}\left(1 - \sin\dfrac{3\theta}{2}\right)}{3lH\cos\dfrac{\theta}{2}} + \frac{2\sigma}{(\rho_l - \rho_g)g}HR_0\right] \quad \ldots\ldots(2).$$

From both (1) and (2) the angle of contact can be determined.

Dorsey (*J. Wash. Acad. Sci.* XVIII. 505, 1928) employs with the aid of tables computed by Bashforth and Adams (*An Attempt to test the Theories of Capillary Action*, 1883) an equation of the form

$$\frac{\sigma}{g\,(\rho_l - \rho_g)} = l^2\left[\frac{0{\cdot}05200}{f} - 0{\cdot}12268 + 0{\cdot}0481f\right],$$

where $f = \dfrac{l_1 - h_1}{l} - 0{\cdot}4142$; l_1 and h_1 corresponding to the half width and depth of a drop to a plane parallel to the resting surface so that a tangent to the drop surface makes an angle of 55° with the plane.

This equation is claimed to be accurate to at least 0·1 % if l^2 lies between $1{\cdot}8\left(\dfrac{\sigma}{g\,(\rho_l - \rho_g)}\right)^2$ and $10\left(\dfrac{\sigma}{g\,(\rho_l - \rho_g)}\right)^2$ (for water at room temperatures $2l$ would $= 1{\cdot}7$ cm.).

As a rough approximation the term in brackets in (2) can be equated to unity and we obtain $\dfrac{(\rho_l - \rho_g)gH^2}{2\sigma} = 2\cos^2\dfrac{\theta}{2} = 1 + \cos\theta$. Thus from a knowledge of the lens thickness H and of the surface tension σ, an approximate value of the wetting angle may be determined.

Bashforth and Adams (*An Attempt to test the Theories of Capillary Action*, 1883) studied the effect of increasing the drop size and found that H approached constancy as the drop increased in radius from 0·2 to 0·4 cm. Drops of 0·75 cm. radius are a convenient size.

The method has been employed by Siedentopf (*Wied. Ann.* LXI. 235, 1897) and Langmuir (*Trans. Farad. Soc.* XV. 10, 1920), who used the approximate equation given above. The lens size varied from 1·5 to 2·5 cm. in diameter and some of the values obtained by Langmuir are given in the following table:

Surface	Angle of contact	
	Water $\sigma = 72{\cdot}8$	Water saturated with oleic acid $\sigma = 42{\cdot}8$
	°	°
Mica	18	24
Quartz	—	31
Glass	45	42
Platinum	65	72
Calcite	70	—
Sphalerite	82	82
Galena	86	106
Paraffin	110	—

If $\cos\theta = 0$ we obtain $(\rho_l - \rho_g)\, gH^2 = 2\sigma$, a relationship employed by Richards and Boyer (*J.A.C.S.* XLIII. 274, 1921) and Iredale (*Phil. Mag.* XLIV. 603, 1925) for the determination of the surface tensions of a number of liquids in the form of lenses on a glass surface.

From what has been said, however, the ensurement of zero angle of contact even for liquids which really wet solids is a difficult matter and the method cannot be relied upon for the determination of surface tensions. In moving a lens of liquid over a surface with which it does not form a zero angle of contact it is found that the angles of contact of the receding and advancing portions of the lens are widely different. Thus Ablett (*Phil. Mag.* XLVI. 244, 1923) found by a dynamic method for the angle between wax and water 96° 20′ for the receding and 104° 34′ for the advancing water solid interface, indicating from (1), p. 5, that the surface energy $\sigma_{\text{wet wax}}$ air must be greater than $\sigma_{\text{dry wax}}$ air. Taking the surface tension of water as 74·3 dynes per cm.

in Ablett's experiments, the increase in surface energy of the wax on wetting is some 21 dynes per cm. Sulman (*Trans. Inst. Min. Met.* Nov. 1920) has determined these extreme values of the angle of contact of water in contact with the fresh and with the previously wetted surfaces of a number of minerals; some of his values are indicated below.

Surface	Contact angles	
	Minimum	Maximum
	°	°
Quartz	19·5	58·5
Calcite	39·6	85·5
Galena (1)	35·0	73·0
(2)	41·6	70·0
Iron pyrites	25·5	87·0
Stibnite	24·0	62·8
Garnet	58·2	94·5

Ferguson (*Phil. Mag.* XXX. 633, 1915; see also Nietz, *J.P.C.* XXXII. 255, 620, 1928; Bigelow and Hunter, *J.P.C.* XV. 367, 1911) confirms Magie's (*Phil. Mag.* Aug. 1888) results that the wetting angle which many organic liquids make with glass is not actually zero as is frequently assumed, but although small is finite and reproducible; he gives values of 16° for ether and 17° for turpentine.

The Anchor-ring Method.

On account of its ease of manipulation, the measurement of the surface tension of a liquid from a determination of the maximum pull exerted at the moment of detachment of a thin ring of platinum from the surface has been frequently employed. The experimental apparatus usually employed consists essentially of a hanging platinum ring attached to a torsion wire or chainomatic balance. In speed it leaves nothing to be desired and in vessels of diameter wide relative to that of the ring reproducible results are readily obtained. This method is naturally only applicable to liquids which wet the wire. Whilst the equation employed by Timberg (*Wied. Ann.* XXX. 545, 1887) and later modified by Nietz and Lambert (*J.P.C.* XXXIII. 33, 1929) between the pull on the ring F, the radius R, the wire diameter 2δ, the surface tension σ, and wetting angle θ,

$$(1+\cos\theta)^n \,.\, \sigma = \frac{F}{2\pi R + 2\pi(R+2\delta)},$$

is frequently employed, the results obtained are liable to be in serious error since the pull on the ring is affected in a more complex manner than that indicated by the simple equation, both by the radius and thickness of the ring wire.

Sondhauss (*Ann. Phys. Chem.* VIII. 266, 1878) and Johlin (*Science*, XXIII, 93, 1926) have shown that rings of large diameter (6 cm.) gave values somewhat higher than those of smaller diameter (4 cm.). Similar investigations as to the effect of wire diameter on the values obtained have been made by Edser (*Fourth Report Coll. Chem.* 284, 1922), Klopsteg (*Science*, LX. 319, 1924), and MacDougall (*ibid.* LXIII. 93, 1926). Harkins, Young and Cheng (*ibid.* LXIV. 333, 1926) have shown that the actual volume of liquid (V) lifted by the ring at the moment of detachment is an important factor to be considered for accurate determination of the surface tension, and have made a series of experimental determinations of the necessary correction factors showing the variation in F with R^3/V for different fixed values of the ratio δ/R.

Cary and Rideal (*Proc. Roy. Soc.* A, CIX. 307, 1925) found that accurate comparable results could be obtained more readily by raising the ring to a definite height above the liquid surface without fracture of the ring of liquid adhering to the ring than by actually pulling the anchor ring from off the surface.

Verschaffelt (*Koninkl. Akad. Amsterdam Proc.* XXI. 836, 1919) has examined the problem of the pull exerted on a thin ring of rectangular cross section, and the general theory of the process of detachment has been investigated by Lenard (*Ann. d. Physik.* LXXIV. 381, 1924) and Tichanowsky (*Physik. Zeit.* XXV. 299, 1924; XXVI. 522, 1925).

6. Dynamic methods.

Two dynamic methods have been developed for measurement of the surface tensions, the method of ripples first employed by

Rayleigh (*Phil. Mag.* (5), XXX. 386, 1890) and the vibrating jet method developed by Bohr (*Phil. Trans.* A, CCIX. 281, 1909).

In the ripple method a series of ripples is caused to travel over the surface of the liquid, the ripples being formed by means of an oscillating glass plate attached to an electrically driven tuning fork dipping into the liquid. If viewed by means of intermittent illumination conveniently arranged by periodic interception of the light by interposition of a screen attached to one limb of the fork, apparently stationary waves may be observed and the mean wave length readily determined.

The velocity of propagation of the ripple depends on the surface tension of the liquid. Kelvin (*Phil. Mag.* (4), XLII. 362, 1871) and Rayleigh (*Phil. Mag.* XXX. 386, 1890) showed that the velocity of a ripple moving over a horizontal layer of liquid of surface tension σ was expressed by means of the equation

$$v^2 = \frac{\lambda g}{2\pi} + \frac{2\pi\sigma}{\lambda\rho},$$

where λ is the wave length of the ripple.

If the time of vibration of the tuning fork be τ, then

$$\tau = \frac{\lambda}{v},$$

whence

$$\sigma = \rho \left\{ \frac{\lambda^3}{2\pi\tau^2} - \frac{g\lambda^2}{4\pi^2} \right\} *.$$

The method has been employed by Dorsey (*Phys. Rev.* V. 213, 1897) and Grünmach (*Ann. d. Physik*, XXXVIII. 1018, 1912) for the determination of the surface tension of a number of salt solutions. Measurements must not be made too near the wave generator. Dorsey advises a distance of not less than 3·5 cm. It will be noted that σ is dependent on the cube of the wave length, a factor militating against the general adoption of this method for the accurate determination of the surface tension. Again it is a difficult matter to decide how far such a method really yields a true value for the dynamic surface tension.

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* Kelvin's equation $\sigma = \frac{(\rho_1 + \rho_2)\lambda^3}{2\pi\tau^2} \coth \frac{2\pi l}{\lambda} - \frac{(\rho_1 - \rho_2) g\lambda^2}{4\pi^2}$, where ρ_1, ρ_2 are the densities of the two fluids on each side of the interface and l the depth of the liquid, is applicable in shallow troughs.

As we shall have occasion to note in dealing with solutions, the composition of the surface phase is very different from that of the bulk liquid. When a liquid interface is newly formed the system is unstable until the surface phase has acquired its correct excess or deficit of solute by diffusion from or into the bulk of the solution. This process of diffusion is by no means instantaneous and, as has been observed in discussing the drop weight method, several minutes may elapse before equilibrium is established. In the ripple method the surface is not renewed instantaneously but may be regarded as undergoing a series of expansions and contractions; thus we should anticipate that the value of the surface tension of a solution determined by this method would lie between those determined by the static and an ideal dynamic method respectively.

More closely approaching the conditions desirable for determining the true dynamic surface tension is the vibrating jet method.

If a stream of liquid be forced through a small jet of elliptical cross section, it will be observed that the issuing jet is in apparent vibration and forms a series of nodes equidistant from one another. From a determination of the wave length of the vibration, a measurement which can be made with some accuracy provided that the stream of liquid issues at a constant speed, the surface tension of the liquid may be determined by means of the following equation developed by Bohr (*Phil. Trans.* A, CCIX. 281, 1909).

If v be the velocity of outflow, $r_{\text{max.}}$, $r_{\text{min.}}$ the semi-major and minor axes of the jet, a the mean radius, $\frac{b}{a}$ the amplitude $= \frac{r_{\text{max.}} - r_{\text{min.}}}{r_{\text{max.}} + r_{\text{min.}}}$, ρ the density of the liquid and σ its surface tension, ρ_1 the density of the gas above the liquid, λ the wave length, and η the viscosity of the liquid, Bohr showed that

$$\sigma = \frac{4\pi^2}{\lambda^2} v^2 a^3 (\rho + \rho_1) \frac{\left[1 + \frac{37}{24}\left(\frac{b}{a}\right)^2\right]}{\left[6 + 10\left(\frac{\pi a}{\lambda}\right)^2 + 2{\cdot}5\left(\frac{\pi a}{\lambda}\right)^4\right]} \cdot \left[1 + \frac{\eta\lambda}{\rho v a^2 \pi} + \ldots\right]^{\frac{3}{2}}.$$

The term $\left[1 + \frac{\eta\lambda}{\rho v a^2 \pi} + \ldots\right]^{\frac{3}{2}}$ however, even in 23 % cane sugar solution, is only 1·0002 and can therefore be considered as unity.

This method has been employed by Schmidt (*Zeit. Physikal. Chem.* XXXIX. 1108, 1912) for determining the surface tension of amalgams and by Stocker (*Zeit. Physikal. Chem.* XCIV. 149, 1920) for solutions with satisfactory results.

The determination of surface tensions at high temperatures.

The method of the sessile drop has been applied by several investigators, notably Quincke (*Pogg. Ann.* CXXXIV. 356, 1868; CXXXV. 261, 1869; CXXXVIII. 141, 1870; CXXXIX. 1, 1871), Siedentopf (*Ann. d. Phys.* LXI. 235, 1897), and Heydweiller (*Ann. d. Phys.* LXII. 694, 1897; LXV. 311, 1898). On account of the lack of knowledge both of the contact angles and of the changes in shape on solidification, the results of this method cannot be claimed as very accurate.

Metal	Temperature ° C.	σ dynes per cm.	Metal	Temperature ° C.	σ dynes per cm.
Tin	299	527	Bismuth	300	388
	401	526		400	380
	600	525		600	367
	800	520		962	340
	964	514	Cadmium	330	570
Lead	380	453		400	597
	400	446		500	591
	600	436		600	585
	800	425	Antimony	640	380
	982	414		700	349
				800	346
				970	342

Grünmach (*Ann. d. Phys.* III. 660, 1900) has employed the ripple method, whilst Smith (*Jour. Inst. Met.* XIII. 168, 1914) measured the capillary depression of the metal in a carbon tube and assumed in all cases that the angle of contact was 180° C. More accurate results have been obtained by Jäger's method of maximum bubble pressure employed by Hogness (*J.A.C.S.* XLIII. 1621, 1921) for the metals mercury, tin, lead, bismuth, cadmium and zinc, and by Bircumshaw (*Phil. Mag.* I. 342, 1926). Fused silica tubes are employed, two tubes of different radii being immersed in the liquid metal to the same depth and the surface tensions calculated from the difference in pressures necessary to evolve a constant but slow stream of bubbles of hydrogen from their orifices. Some of Bircumshaw's values are given above.

Static and dynamic surface tension.

The static methods of measuring surface tension lead to values of this quantity for a surface which has been in existence for a considerable period of time, varying from a minute or less, when the drop-weight method is used upwards. The different static methods appear as a rule to lead to similar results for the surface or interfacial tension of the same liquid. Dynamic methods measure the tension of a surface which must necessarily have existed for a much shorter period of time before the determination: for example, in the vibrating jet method the age of the surface may be as little as 0·01 second, while by a modification of the capillary rise method due to Lenard and His (*Heidelberg Akad. Wiss.* XXVIII. 16, 1914), the tension may be investigated of a surface whose age is not more than 0·001 second. The dynamic methods give rise to results which differ more among themselves than from those of static methods, and it is natural to assume in explanation of this difference that the equilibrium conditions at the surface have not in all cases been obtained. Further work on the dynamic surface tensions of associated liquids, such as water examined by Lenard (*loc. cit.*) and Schmidt and Steyer (*Ann. d. Phys.* LXXIX. 442, 1926), see also Kleinmann (*ibid.* LXXX. 245, 1926), and of solutions containing solutes of varying diffusivity, should throw light on the important question of the rate of attainment of equilibrium in the surface phase.

7. The total surface energy.

The relationship between surface tension and temperature leads to a series of interesting results bearing upon chemical constitution and the structure of the surface layer. As we have seen, the surface tension is numerically equal to the free surface energy from which with the aid of the temperature coefficient the total surface energy may be obtained.

In the following table a few values of the free surface energies and the temperature coefficients are given.

Liquid	σ_0	$-\frac{d\sigma}{dT}$
Water	75·87	0·1511
Carbon disulphide	37·71	0·1607
Mercury	480·30	0·2330
Hexane	21·31	0·1039
Octane	23·36	0·0920
Chloroform ...	28·77	0·1134
Phenol	42·27	0·1050

Since $\frac{d\sigma}{dT}$ is always negative for pure liquids, the total surface energy is greater than the free energy; moreover, as the surface tension decreases roughly in a linear manner with elevation of the temperature, the total surface energy remains approximately constant over a considerable temperature range and is a convenient quantity to use in the comparison of the surface behaviour of different liquids.

As examples of the magnitude of variation in the free surface energies and the approximate constancy of the total surface energies, the following data for benzene (Whittaker, *Proc. Roy. Soc.* A, LXXXI. 21, 1900), mercury and carbon tetrachloride (Harkins and Roberts, *J.A.C.S.* XLIV. 656, 1922) may be cited (see tables, p. 27).

A critical examination of the total surface energies of various liquids has been made by Langmuir and Harkins. It is found that the surface energies of the aliphatic hydrocarbons are mainly independent of the length of the hydrocarbon chain, whilst the surface energies of the alcohols are but slightly larger than those of the corresponding hydrocarbons. Langmuir in his investigations on the behaviour of thin films of insoluble fatty acids and alcohols on the surface of water (Ch. III) came to the conclusion that such molecules were orientated in the surface with their hydrocarbon chains in the gas phase and their polar carboxyl or hydroxyl groups in the water phase. If we assume a similar orientation of the surface film of a homogeneous liquid and that the surface energy is defined by the nature of the surface film alone, the experimental facts may be interpreted at least in a qualitative way. For hydrocarbons will expose the methyl groups at the ends of the chains to the air, whilst fatty acids and alcohols will likewise possess a surface layer of CH_3 groups, the polar —COOH and —OH being immersed in the bulk of the liquid. We thus arrive at a hypothesis as to the structure of the surface phase for pure liquids, that it consists of a layer of orientated molecules with the active portions of the molecule drawn inwards and that the total surface energy is determined by the nature of the external groups of the molecules. It is probable however that this assumption whilst expressing the limiting ideal conditions of such a surface film does not represent the properties of actual films.

Benzene			
Temp. ° K.	σ ergs per sq. cm.	$\frac{d\sigma}{dT}$	U ergs per sq. cm.
353	20·28	– 0·111	59·5
363	19·16	– 0·113	60·2
373	18·02	– 0·115	60·9
383	16·85	– 0·1155	61·1
393	15·71	– 0·1145	60·7
413	13·45	– 0·111	59·4
433	11·29	– 0·108	58·0
453	9·15	– 0·104	56·1
473	7·17	– 0·099	54·0
493	5·25	– 0·094	51·5
513	3·41	– 0·087	48·1

Mercury			
Temp. ° K.	σ ergs per sq. cm.	$\frac{d\sigma}{dT}$	U ergs per sq. cm.
313	479·7	– ·233	552·6
363	468·0	– ·233	552·6
413	456·4	– ·233	552·6
443	449·4	– ·233	552·6
Carbon tetrachloride			
313	24·41	– ·117	60·87
413	12·22	– ·103	54·80
463	7·28	– ·095	51·26
503	3·56	– ·087	47·30
523	1·93	– ·076	41·68
533	1·20	– ·067	36·91

In the case of water for example we must assume on this hypothesis a layer of orientated molecules on the surface of the liquid. The surface molecules however are continually evaporating and recondensing on the surface. The rate of evaporation and condensation may readily be determined with the aid of the Herz-Knudsen effusion equation (see p. 194)

$$\mu = \frac{KP}{\sqrt{MT}},$$

where μ is the rate of effusion, P the vapour pressure and M the molecular weight. At 20° C. the rate of evaporation is some 10^{22} molecules per sq. cm. per second or the life of a molecule on the surface is only 10^{-7} seconds. During this small period of time the molecule must become orientated and assume a vertical posture about which mean position it must oscillate. This order of time although small does not necessarily necessitate a rejection of the hypothesis for the moment of inertia of a water molecule is extremely small*.

The other assumption that the total surface energy is determined by the nature of the external groups of the molecules is capable of more direct proof. We find for example that the total surface energy increases in aliphatic compounds as H is replaced in the order: OH, NH_2, CN, I, SH, COOH, NO_2, $COOCH_3$, COCl, $CONH_2$. Evidently the assumption is not strictly true, for these substituent groups should not affect the surface tension of a hydrocarbon, CH_3, surface. Langmuir assumes that these larger groups force apart the surface molecules and that the forcing apart of these groups increases the surface energy.

Langmuir and Harkins from an examination of the total surface energy of benzene and substituted derivatives came to the conclusion that this molecule lay as a flat ring on the surface, but by the introduction of a polar group the ring was tilted on edge causing a rise in the surface energy, according to Harkins by permitting the residual valencies of the carbon atoms in the ring to come into play. An alternative suggestion is that owing to the tilt more molecules can be accommodated on the surface. Harkins further attempts to explain the differences of behaviour between the ortho- and para-compounds in various cases by similar assumptions, which do not seem to be in close accord with the experiments. (See also King and Wimpler, *J.A.C.S.* XLIV. 1894, 1922.)

Sugden (*J.C.S.* CXXV. 1167, 1924) has examined the total surface energies of a number of para-substituted benzene compounds. If these compounds are orientated so that the surface molecules are perpendicular to the surface, the area occupied by each molecule is simply that of the cross section of the benzene ring. This avoids the complication that different molecules might occupy different areas. If we take a series of para-compounds $X\phi Y_1$, $X\phi Y_2$, ... $X\phi Y_6$, the groups Y_1—Y_6 having progressive residual affinities, the residual affinity of the group X lying between Y_3 and Y_4, the molecules should orientate themselves in the following manner:

---

* The natural period of a molecule as determined from both the thermal conductivity and from the natural infra-red vibration frequency is of the order of 10^{-12} seconds.

Y_1	Y_2	Y_3	X	X	X	Vapour
X	X	X	Y_4	Y_5	Y_6	Liquid

and the surface energies of the first three compounds should progressively increase whilst those of compounds 4, 5, 6 should be identical.

Further, if we take a series $Y_2\phi Y_1$, $Y_2\phi Y_3$, $Y_2\phi Y_4$, none of these compounds should have a surface energy greater than that of $Y_2\phi Y_3$ or $X\phi Y_2$, since Y_2 is the greatest residual affinity which is lifted into the surface. The following values are taken from Sugden's paper:

Y	CH_3	H	Cl	Br	I	NO_2	NH_2
$X = H$	65·53	70·26	71·01	74·48	77·07	81·70	82·40
$= Cl$	66·65	71·01	71·45	71·83	74·71	78·68	81·37
$= CH_3$	—	65·53	66·65	66·46	69·28	74·06	68·19

On the strict theory of orientation, the data in the first horizontal series must be interpreted on the assumption that the substituent groups are all in the vapour phase, the hydrogen being in the liquid, a conclusion quite opposite to that usually obtained. In the second and third series according to the above reasoning the surface energy of chlorbenzene and toluene should have been the respective maxima.

We must conclude that the surface tension of a pure liquid is determined by properties of the molecule as a whole together with its foundation rather than by the external groups only.

In the case of solutions also, Goard has noted that in phenol solutions possessing identical surface concentrations of phenol the surface tension varies with the nature of the underlying bulk phase, being higher for solutions containing salt (see p. 55).

8. The surface energy and latent heat of evaporation.

Many attempts have been made to correlate the latent heat of evaporation of a liquid and its surface tension (see Edser, *Fourth Report on Colloid Chemistry*). The process of evaporation may be considered to take place in two stages. In the first it is brought from the interior to the surface overcoming the surface tension, in the second it vaporises from the surface film. According to Laplace's theory of a diffuse gradient of properties between bulk liquid and vapour, we should anticipate that the molar surface energy should be half the molar internal latent heat, a generalisation known as Stefan's law (*Wied. Ann.* XXIX. 655, 1896). On the conception however of a discrete surface of separation it is evident that this should not be the case, for a molecule proceeding from the interior to the surface requires the supply of sufficient energy to remove the non-polar end of the molecule from the liquid to the vapour phase, it being still attached by the polar end to the bulk liquid phase. The second process of superficial vaporisation entails the separation of the active group from the liquid.

Liquid	Corresponding temperature 0·7 of T_c. ϵ total surface energy per molecule $\times 10^{14}$ ergs	λ internal latent heat of vaporisation per molecule $\times 10^{14}$ ergs	$j = \lambda - \epsilon$ energy changed from potential to kinetic when molecule jumps from surface to vapour, per molecule $\times 10^{14}$ ergs	$\frac{\epsilon}{\lambda}$
Nitrogen	3·84	8·7	4·8	0·514
Carbon tetrachloride	18·2	40·2	22·0	0·452
Benzene	18·4	41·7	23·3	0·441
Chlorbenzene ...	20·3	48·8	28·5	0·417
Ethyl alcohol ...	11·2	59·3	48·1	0·186
Methyl alcohol ...	8·5	51·6	43·1	0·164

Clearly equality between the two stages in the process of evaporation from the interior of the liquid should only obtain for perfectly symmetrical molecules; with increasing asymmetry, the second step or the detachment of the polar end of the molecule should become more important and the energy associated with this rupture will be a larger fraction of the total energy of vaporisation. An examination of the surface energy and latent heats of evaporation for a series of compounds at corresponding temperatures has been made by Harkins and Roberts (*J.A.C.S.* XLIV. 653, 1922), some of whose results are given in the table above.

It will be noted that the symmetrical compound carbon tetrachloride differs markedly in the ratio $\frac{\epsilon}{\lambda}$ from the unsymmetrical methyl alcohol.

The principle of independent surface action.

Whilst it is clear that the total surface energy of a liquid consisting of complex organic molecules is not determined completely from the concept of a layer of orientated molecules exposing their least active groups to the air liquid interface, yet the evidence presented from surface tension data confirm the view that the characteristics of such molecules as a whole are largely determined by "group" properties. We may note for example, in addition to the case of the latent heat of evaporation just cited, the influence of polar groups on solubilities of substances in polar solvents or the effects of substitution of polar groups on the electric moments of molecules. Sir W. B. Hardy (*Proc. Roy. Soc.* 1913) based the conception of molecular orientation at a surface on the existence of unsymmetrical fields of force surrounding the molecules, whilst Langmuir (*J.A.C.S.* XXXVIII. 2222, 1916; *Colloid Symposium Monograph*, III. 48, 1925) extended this concept very materially by identifying these unsymmetrical fields with the presence of specific groups in the molecule. This identification has led to the enumeration of the principle of independent surface action, that the field of force about a particular group or radical in a large organic molecule is characteristic of that group and as a first approximation is independent of the nature of the rest of the molecule. The principle cannot be regarded as at all strict. Thus on the insertion of two polar groups into the same molecule, although in some cases the resultant electric moment may be calculated from the vectorial sum of the individual moments, this is by no means general. Again, in the aliphatic dibasic acids the mutual interaction of the two groups as shown from the dissociation constants is quite marked even when the groups are separated by as many as five carbon atoms of a straight or coiled chain.

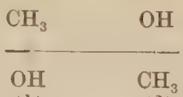
Whilst the mutual interaction of molecules to form associated liquids is characterised by a large change in the molecular electric moment, the electric moment being determined chiefly by the presence of polar groups to which the association is due, yet the parallelism between the association factor and the change in molecular electric moment on concentration is only superficial. Finally, although the electric moments ascribed to polar groups is high, there is no quantitative relationship between the values of these and those of the total group surface energies.

Langmuir (*loc. cit.*) has applied the principle of independent surface action to a consideration both of the orientation of molecules at surfaces as well as the vapour pressures of substances and binary mixtures with the aid of the generalised Boltzmann equation

$$\frac{n_1}{n_2} = \frac{P_1}{P_2} = \frac{p_1}{p_2} e^{\frac{\phi}{kT}},$$

where n_1 and n_2 are the numbers of molecules per unit volume in two regions in equilibrium with one another but differentiated from one another by requiring the expenditure of potential energy ϕ in moving a molecule from one region to the other. If we consider not two regions but two states of the matter, P_1 and P_2 are the actual probabilities per unit volume of the existence of the molecules in the two states. The *a priori* probabilities p_1 and p_2 vary but little with the temperature and are dependent upon geometrical factors and quantum restrictions.

We may apply the principle to the case of the surface distribution of methyl alcohol molecules in the free surface of the liquid. The two possible states with the maximum difference of energy between them can be depicted as follows:



$$\begin{array}{cc} CH_3 & OH \\ \hline OH & CH_3 \\ (1) & (2) \end{array}$$

if A be the area of the molecule and U_{CH_3}, U_{OH}, U_x be the total surface and interfacial energies of the constituent groups—CH_3 and OH. The total surface energy in position (1) is $\frac{1}{2}A\ (U_{CH_3} + U_x)$ and in (2) is similarly $\frac{1}{2}A\ (U_{OH} + U_x)$. Thus the difference in energy which is available for causing orientation is $\phi = \frac{1}{2}A\ (U_{CH_3} - U_{OH})$.

Inserting the values $A = 65$ Å., $U_{CH_3} = 337$ and $U_{OH} = 190$, we obtain $\phi = 5{\cdot}1 \,.\, 10^{-13}$ ergs.

For a value of $T = 293°$ K. we find $kT = 4{\cdot}0 \,.\, 10^{-14}$ ergs; thus the exponent is 13, giving a probability ratio in favour of the first orientation of several hundred thousand. The limitations of this method are discussed in detail by Smyth and Engel (*J.A.C.S.* LI. 2646, 2660, 1929).

9. The influence of temperature on the surface tension of liquids.

The surface tension of all liquids decreases as the temperature rises. Over small ranges of temperature the relationship is with few exceptions linear

$$\frac{d\sigma}{dT} = -K$$

or

$$\sigma_t = \sigma_0\,(1 - \alpha T),$$

where

$$K = \alpha\sigma_0.$$

At the critical temperature the distinction between the two phases and consequently the surface tension disappear. The absolute magnitude of the surface tension therefore depends to a great extent upon the distance from the temperature of observation to the critical point; thus we find that while the permanent gases have tensions never exceeding a few dynes per cm., in the case of liquefied metals the surface tensions may exceed a thousand.

Ramsay and Shields and Walden concluded from their experiments that a linear relation held almost up to the critical point and write

$$\sigma = c\,(T_c - T - \delta),$$

where T_c and T are the critical and observation temperatures, c and δ constants. Van der Waals in his theory of capillarity developed the equation

$$\sigma = \sigma_0\left(1 - \frac{T}{T_c}\right)^{\frac{3}{2}}.$$

Hence $$\frac{1}{\sigma_0}\frac{d\sigma}{dT} = \frac{3}{2}\sqrt{1 - \frac{T}{T_c}} \times \left(-\frac{1}{T_c}\right),$$

and $\frac{d\sigma}{dT}$ vanishes with σ at the critical point. Experiment however agrees better with a modified formula

$$\sigma = \sigma_0\left(1 - \frac{T}{T_c}\right)^n,$$

where n varies somewhat for different liquids but is in the neighbourhood of 1·21 as determined by Ferguson (*Trans. Farad. Soc.* XIX. 408, 1923).

10. The Eötvös' Law.

The variation of surface tension with the temperature has been studied by many observers with the view of testing the theory of Eötvös that the molar free surface energy of any liquid should be proportional to the distance from its critical temperature and to a universal constant, a "law" analogous to the gas law $PV = RT$, the product PV being the free molar volume energy of the gas. Correspondingly in the case of the liquid-vapour surface, the molar free energy is proportional to the product of σ and the surface occupied by a gram molecule or to $\sigma\left(\frac{M}{\rho}\right)^{\frac{2}{3}}$, where M is the molecular weight and ρ the density of the liquid. (On the assumption that the molecules are symmetrical in shape.)

Instead of T we write $T_c - T$ and obtain

$$\sigma\left(\frac{M}{\rho}\right)^{\frac{2}{3}} = K\,(T_c - T),$$

where K is a universal constant of approximate value 2·2.

Ramsay and Shields tested this relation for a large number of liquids and modified it to $\sigma\left(\frac{M}{\rho}\right)^{\frac{2}{3}} = K(T_c - T - \delta)$, since the molar surface energy appeared to vanish at a temperature somewhat below the critical point.

To avoid the necessity for determining the critical temperature we may differentiate and write

$$K = \frac{d}{dT}\left\{\sigma\left(\frac{M}{\rho}\right)^{\frac{2}{3}}\right\},$$

or assuming that M is independent of the temperature (i.e. for non-associated liquids)

$$K = M^{\frac{2}{3}}\frac{d}{dT}(\sigma\rho^{-\frac{2}{3}}).$$

Katayama (*Tokio Univ. Sci. Rep.* IV. 5. 373, 1916) examined an equation of the type

$$\sigma\frac{M^{\frac{2}{3}}}{(\rho_l - \rho_v)^{\frac{2}{3}}} = K(T_c - T),$$

and showed that this represented the results of experiment over the full range of temperature from freezing to critical point which Ramsay's equation even when modified fails to do.

An examination of the data however indicates that the constant K of Eötvös' equation is by no means a universal constant of mean value 2·2, as is revealed by the following table:

Less than 2·2		Greater than 2·2	
Liquid	K	Liquid	K
Ethyl alcohol ...	1·08	Methylbenzoate ...	2·32
Acetonitrile ...	1·44	Paraldehyde	2·37
Propyl alcohol ...	1·40	Phenetole	2·56
Amyl alcohol ...	1·35	Phenylisosulphocyanate	2·32
n-Butyric acid ...	1·57	Diethylaniline	2·337
Iso-butyric acid	1·66	Diphenylamine ...	2·57
Acetic acid ...	0·95	Dimethyl-o-toluidine ...	2·49
Glycol	1·03	Benzophenone	2·63
Caproic acid ...	1·62	Anisole	2·358
Phenol ...	1·70	Quinoline	2·43
p-Tolunitrile ...	1·72	Ethyl esters of	
		Propionylmalic acid ...	2·87
		Butyrylmalic ,, ...	3·18
		Valerylmalic ,, ...	3·40
		Caproylmalic ,, ...	3·04
		Pelargonylmalic ,, ...	3·68
		Capronylmalic ,, ...	3·59

For a considerable group the temperature coefficient of the molecular surface energy $\frac{d}{dT}\left\{\sigma\left(\frac{M}{\rho}\right)^{\frac{2}{3}}\right\}$ is found to be in the neighbourhood of 2·2: this group included the saturated hydrocarbons, liquids which of all others would be expected to exist as simple unassociated molecules. (For argon, nitrogen, and carbon monoxide, Baly and Donnan found values of K very close to 2·0.)

In a second group, which includes water, the lower fatty acids and alcohols, amines, nitriles and phenols, values of K considerably below 2·2 are found. Since other grounds, such as abnormal coefficients of expansion and specific inductive capacity, indicate that these substances are probably associated to some extent, Ramsay and Shields attempted to bring the coefficients of molecular surface energy into line with those of the first group by replacing M, the formula weight, by αM, where α is the degree of association and αM therefore the mean molecular weight. In this procedure it is assumed that the average composition of the surface layer is the same as that of the liquid in bulk, for otherwise the value of α obtained can apply only to the surface layer. In order to decide this question, Ramsay and Aston examined the surface tensions at different temperatures of mixtures of organic liquids of different molecular weights, and compared the values of K for the mixture in each case with that calculated from the K of the components and their molecular proportions in the mixture. The calculated and observed values of K agreed within the limits of experimental error and it was concluded that the assumption made was justified. Unfortunately, however, the examples chosen are not sufficient to prove the case, for in no example do the surface tensions of the liquids differ by more than six dynes per centimetre, so that little deviation from a simple mixture rule could be expected. If instead of two organic liquids with not very different surface tensions the experiment had been carried out with water and an alcohol, a different conclusion would have been reached. Undoubtedly the mean molecular weights in the surface and the liquid differ greatly in such a case. Now where we are dealing with a simple liquid and its polymeric modification we should expect to find that the order of difference between their surface tensions in an imaginary pure state would be large; in order to illustrate this point the example of Walker (*Phil. Mag.* XLVII. 111, 1924) will be followed by constructing a table of surface tensions of pairs of compounds, one in each pair having approximately twice as large a nucleus as the other.

Temp. °C.	Liquid 1	σ_1	Liquid 2	σ_2
129·2	Benzene	14·71	Diphenyl	28·64
108·3	Toluene	19·6	Dibenzyl	27·86
− 39·1	Propane	14·95	Hexane (extrapolated)	22·76
20	*i*-Pentane... ...	13·72	Di-isoamyl	22·24
20	Methylene chloride	26·52	Acetylene tetrachloride	34·1
24·9	Ethyl formate ...	22·9	Ethyl oxalate... ...	31·4
0	Amyl acetate ...	26·6	Amyl succinate ...	30·9

In an extreme case the surface tension of diphenyl is almost double that of benzene at the same temperature, and it would be expected that in a mixture of these substances the benzene would be preferentially adsorbed at the surface, and any attempt to find the mean molecular weight of the two would break down. Certain mixtures of aniline and water were found by Worley (*J.C.S.* CV. 260, 1914) to have positive temperature coefficients of surface tension as exemplified in the following data for a 3·3% aniline solution; this would lead to a mean molecular weight less than zero. Such criticisms suggest that although a deviation below the normal value of K does indeed indicate that there is association, the degree to which it occurs cannot be obtained as simply as was assumed.

Temp. ...	15° C.	55° C.	95° C.
σ ...	48·21	49·22	50·73 dynes per cm.

Another amendment to the simple rule of Eötvös is made necessary owing to the existence of a third class of bodies with exceptionally high values of K. Such for example are the higher fatty acids and their glycerides, investigated by Walden. We cannot assume dissociation in the pure liquid state, for even when dissolved in dissociating media there is no physical evidence of it. The simplest explanation in harmony with the theory of

Eötvös is furnished by the observation that bodies of this third class possess in all cases long chains of atoms so that the molecule must present a highly unsymmetrical appearance. The molecular surface will, if the molecules lie flat in the superficial layer, considerably exceed the calculated amount $\left(\frac{M}{\rho}\right)^{\frac{2}{3}}$, and if they are orientated normally to the surface, fall much below this value. In the first case the calculated K would be lower and in the second higher than the normal value. This explanation is in harmony with other observed facts concerning long chain compounds, such as their tendency to form "liquid crystals," their orientation towards a water-air surface and the formation of micelles. When interpreting the observed values of K attention must be paid to the shape of the molecule and its orientation as well as to its state of association*.

Allusion has already been made to the Eötvös constants of liquids at low temperatures which are rather less in the cases quoted than the normal value for ordinary temperatures although there is very little probability of association, more especially in the case of argon. At still lower temperatures K. Onnes has found K for hydrogen to be 1·4, so that this coefficient diminishes as the absolute zero is approached. For helium an abnormally low value for K is found.

Low values pointing to association are likewise found for the liquid metals (Harkins and Ewing, *J.A.C.S.* XLII. 2539; Bircumshaw, *Phil. Mag.* III. 1292, 1927). Thus we obtain for mercury 0·96, lead 0·22, bismuth 0·27, antimony 0·02.

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* Conversely, from a knowledge of the value of K for an unassociated substance, conclusions may fairly be drawn as to the shape and orientation of its molecule, subject of course to limitations imposed by thermal agitation in the surface. For example, the value of K for the glycerides of oleic and palmitic acids reaches 6, or three times the normal value. If orientation is completely normal to the surface, this would correspond with a length some five times the diameter—much about what we should expect of these bodies if the three hydrocarbon chains lay parallel. The free acids have a much smaller K, and since the ratio of length to diameter in their case must be even greater than for the glycerides we must conclude that there is far less orientation, and that the shape of the molecule allows more molecules to come into a given space of surface in a random disposition than would be the case for a molecule of the same volume but of regular shape.

It would be of much interest to have data for liquids whose molecules may with certainty be assumed spherical in form and not at all associated, for example of methane, tetramethylmethane or tricyclobutane. We should expect these liquids to have equal values of K unaffected by temperature, and the common value would provide a starting point, the deviation from which gives a measure of the association or ellipticity of the molecules of other substances.

The Parachor.

Sugden (*J.C.S.* CXXV. 1177, 1924; CXXVII. 1525, 1868, 1925) has compared the molecular volumes of substances under conditions such that they possess identical surface tensions and has shown that they are determined by the molecular constitutions of the substances. In obtaining the "parachor" P, Sugden makes use of the approximate relationship between free surface energy and density noted by Macleod (*Trans. Farad. Soc.* XIX. 38, 1923)

$$\sigma = c\,(\rho_l - \rho_v)^4,$$

where c is a characteristic constant independent of the temperature. The parachor P is $\sqrt[4]{c}\,.\,M$ or

$$P = \frac{\sigma^{\frac{1}{4}}}{(\rho_l - \rho_v)}\,.\,M.$$

P is found to be a function of the chemical constitution, and definite values can be ascribed both to the elements, their ions and to the various types of linkage obtained in organic compounds. The values given by Mumford and Phillips (*J.C.S.* CCLXXIV. 2112, 1929) include the following:

Group	P	Group	P
CH_2	40	P	40·5
C	9·2	As	54
H	15·4	Sb	68
O	20	Triple bond ...	+ 38
S	50	Double bond ...	+ 19
Se	63	Singlet linkage	− 9·5
F	25·5	3-membered ring	+ 12·5
Cl	55	4 ,,	+ 6
Br	69	5 ,,	+ 3
I	90	6 ,,	+ 0·8
N	17·5	7 ,,	− 4

Ring formation is thus attended with a change in molecular volume due to the strain imposed on the molecular linkages. We notice that in accordance with the Bayer strain theory that a six-membered carbon ring suffers the least distortion. The introduction of a group such as $>C{=}O$ into a ring also affects the molecular volume, and gives rise to a positive strain equivalent of about + 3·0 units.

The $>C{=}O$ in aliphatic ketones and aldehydes is unaccompanied by strain, but in carbonates, esters and acid chlorides it introduces a strain equivalent to + 3·0 units and about + 6·0 units in carbonyl chloride.

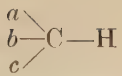
The parachors for a few substances calculated with the aid of the above data are compared with the experimental values in the following table:

Compound	*P* obs.	*P* calc.
C_2H_6	110·5	110·8
nC_8H_{18}	350·3	350·8
$nC_{60}H_{122}$	2480·0	2430·8
Benzene	205·0	205·4
Cyclohexane	239·3	240·8
Cyclopentanone	214·2	214·2
Acetone	161·5	159·0

Chain branching is likewise accompanied by a slight but definite diminution in the parachor, the decrement although varying slightly with the chain length and position is of the order of − 3·0 units.

The apparent atomic parachor like the electric moment between two atoms naturally varies, not only with the valency of the linkage but also with the atomic size and field strength between the atoms; this is readily observed in the atomic parachors for hydrogen in combination with various elements:

Element	*P* for hydrogen
Carbon	15·4
Nitrogen	12·5
Oxygen	10·0
Sulphur	15·4
Chlorine	12·8
Bromine	16·4

We should also anticipate that a union of the type  $\begin{matrix} a \\ b \\ c \end{matrix}\!\!>\!\text{C—H}$ would be affected by the nature of the groups *abc*. The introduction of electro-negative groups into *abc* alters the electric moment of the C—H linkage; the parachor values of $\text{—CH}a_2$ and $\text{—C}a_3$ groups, where *a* is an electro-negative element or group, are likewise some 3 and 6 units less than that of the group $\text{C}a_4$ and no less than 9 units below the value calculated by summation.

11. The vapour pressure above curved liquid surfaces.

The equilibrium vapour pressure over a concave liquid surface must be somewhat less and over a convex surface somewhat greater than that over a plane surface; the quantitative relationship between the curvature of the surface and the alteration in vapour pressure effected by such curvature was first deduced by Lord Kelvin (*Phil. Mag.* (4), XLII. 448, 1881) and may be obtained in the following manner. If we imagine a small mass of liquid δm to be transferred from a drop of radius r_1 to one of radius r_2, the work done by the surface forces will be $\sigma\delta A$, where δA is the decrease in area. If δv, δr and δA be the changes in the volume, radius and surface of one of the drops due to the change of mass δm, then $\delta v = \frac{\delta m}{\rho} = 4\pi r^2 \delta r$ and $\delta A = 8\pi r \delta r = \frac{2\delta m}{\rho r}$. Hence the work done on the transfer is $\frac{2\sigma}{\rho}\delta m \left\{\frac{1}{r_1} - \frac{1}{r_2}\right\}$. This mass of liquid may now be returned to the original drop by isothermal distillation and the energy expended is $\delta m \frac{RT}{M} \log \frac{P_2}{P_1}$, where M is the molecular weight of the vapour and P_2 and P_1 the vapour pressures above each drop. We thus obtain

$$\log \frac{P_2}{P_1} = \frac{2\sigma M}{\rho RT}\left(\frac{1}{r_2} - \frac{1}{r_1}\right).$$

We may note also that the total heat of vaporisation of a liquid from a curved surface must differ from that when vaporisation takes place from a plane surface to the extent of

$$\Delta H = \frac{2M}{\rho r}(u) = \frac{2M}{\rho r}\left(\sigma - T\frac{d\sigma}{dT}\right).$$

An interesting application has been made of the Kelvin equation for the determination of the composition of lead amalgam by Ehrenhaft (*Ann. d. Phys.* LXIII. 773, 1920). For small drops of mercury amalgam to be in equilibrium with a plane surface of liquid mercury, the drops must contain increasingly large quantities of lead to reduce the vapour pressure as the radius decreases. The following data illustrate the results obtained:

Drop radius (cms.)	dp/p %	% lead by weight
10^{-3}	0·049	0·052
10^{-4}	0·49	0·52
10^{-5}	4·9	5·2

We shall have occasion to note that the application of the Kelvin equation for the influence of curvature on surface tension has been extended, notably by Ostwald and Hulett, to the solubility of finely divided crystals (see p. 253).

The applicability of the Kelvin equation to very small drops of liquids or to the effect on the vapour pressure of liquids confined in exceedingly narrow tubes is a matter of great importance in connection with the condensation of vapours on solid surfaces which are normally rough and contain cracks or fissures, only a few molecular diameters in width, the presence of which have been demonstrated by Smekal (*Phys. Zeit.* XXVI. 707, 1925). Kelvin himself believed that when the radius of curvature attained some 10μ the equation was no longer applicable, whilst Freundlich (*Kapillarchemie*) considered that droplets with a radius of the order of the range of molecular action would not obey the law. Patrick and Ebermann (*Jour. Phys. Ann.* XXIX. 227, 1925) have concluded that a vapour converted into a gas by raising the temperature beyond the critical will actually condense in fine capillaries, although more recent direct experiments indicate no change in the critical temperature of a liquid when confined in narrow capillaries. That the vapour pressure above a liquid in an exceedingly narrow capillary tube may be far less than that calculated with the aid of the Kelvin equation is revealed by the experiments of Shereshefsky (*J.A.C.S.* L. 2966, 1928), who has conducted experiments on the filling of capillaries of radius from 2 to 5μ with water and with toluene from their vapours over different solutions. It was found that the condensation occurred with vapour pressures some 0·082 mm. under saturation, whilst the limit imposed by the Kelvin equation varied only, with the size of tube, from 0·009 to 0·049 mm. under saturation.

Bigelow and Trumble (*J.P.C.* XXXI. 1799, 1927) have shown that small drops of mercury on a glass plate distil readily to larger ones, but no effects due to curvature could be obtained with crystals of iodine, naphthalene or camphor. Distillation likewise did not take place from small drops of sulphur or phosphorus, but these substances wet glass and the drops formed on the surface are thus in equilibrium with a film and acquire as we shall note shapes characteristic of the spreading pressures. Distillation from small drops of supercooled sulphur to larger crystals readily took place.

Conclusive evidence for an extended range of molecular action is provided in the investigations of Sir W. Hardy (Hardy and Nottage, *Proc. Roy. Soc.* A, CXVIII. 209, 1928) on adhesion between two plates lubricated with different types of lubricant. It was found that the mutual influence of the plates separated either by lubricant or by air persisted over a relatively wide range of separation. For optically smooth surfaces the limiting distance was found to extend up to some 4 to 5μ.

Capillary Flow.

The dynamics of capillary flow, of importance in the rate of attainment of membrane equilibria, have not been subjected to any very exhaustive examination. Some attention has been paid to the rate of flow of a liquid along a horizontal capillary from a large reservoir under the influence of the surface tension forces alone. Bell and Cameron (*J.P.C.* X. 659, 1906) deduced the relationship between the length of travel and the time

$$\frac{x^2}{t} = \text{constant}.$$

Washburn (*Phys. Rev.* XVII. 276, 1921) examined the problem in more detail and deduced for the conditions of horizontal flow on the assumption of the validity of Poiseuille's law the equation

$$x^2 = \frac{\sigma \cos \theta}{2\eta} rt,$$

where σ is the surface tension, η the viscosity of the liquid and r the capillary radius. Rideal (*Phil. Mag.* XLIV. 1154, 1922) obtained for the flow of a wetting liquid the expression

$$t = \frac{2\eta}{\sigma r} x^2 - \frac{\rho r^2}{8\eta} \log x + \frac{\rho^2 r^5}{512\eta^3 x^2},$$

where ρ is the density of the liquid. For small values of r this reduces to Washburn's form.

The function $\frac{\sigma \cos \theta}{2\eta}$ thus defines the penetrating power of a liquid and may be termed the penetration coefficient.

For a glass capillary tube of $r = 0{\cdot}354$ mm., which had been previously washed out with the liquid under investigation so as to ensure a zero angle of contact, Rideal found the following values for $\sqrt{\frac{\sigma r}{2\eta}}$:

Liquid	$\sqrt{\frac{\sigma r}{2\eta}}$ calc.	$\sqrt{\frac{\sigma r}{2\eta}}$ obs.
Isobutyl alcohol	3·75	3·70
Isopropyl alcohol	4·10	4·20
Ethyl alcohol ...	5·52	5·65
Methyl alcohol...	8·16	7·90
Chloroform ...	8·73	8·60
Benzene ...	8·90	9·90
Ether	11·38	10·95
Water	11·31	11·40

Washburn obtained a wetting angle of 112° for mercury against glass by determination of the penetration coefficient and utilising the accepted data for η and σ, and further showed that the data of Cude and Hulett (*J.A.C.S.* XLII. 391, 1920) on the initial rate of penetration of charcoal by water conformed to this equation.

The pore size of membranes could evidently be determined by this method if a liquid with a zero wetting angle were employed.

The usual methods for the determination of membrane pore size are based upon the capillary rise and on the law of Poiseuille. In the latter method a knowledge of the total pore volume as well as the true length of the capillary in the membrane is required. Bartell (*J.P.C.* XV. 659, 1911; XVI. 318, 1912; XXXII. 1553, 1928), Guérout (*C.R.* LXXV. 1809, 1872), Hitchcock (*J. Gen. Physiol.* IX. 1755, 1926), Duclaux and Errera (*Koll. Zeit.* XXXVIII. 59, 1926) have utilised this latter method.

For packed powder membranes the effective length of the capillary may be taken as approximately $\frac{\pi}{2}$ times the membrane thickness.

In the light of the experimental work on the vapour pressures above fine capillaries already described, it is interesting and somewhat surprising to note that Bartell and his co-workers have obtained almost identical pore sizes by the two methods, both for crushed carbon and quartz.

Bartell and Osterhof (*Coll. Symp.* V. 113, 1928) have measured the pressures required to produce a flow of a number of different liquids through powdered materials as well as the displacement of one liquid by another. The following data may be given as representative of their results with crushed carbon.

The pressure required to displace air by benzene which possesses a zero wetting angle was found to be 6,200 grms./cm.^{2}, thus giving a pore radius of $9{\cdot}3 \,.\, 10^{-6}$ cm. assuming the normal value of $\sigma_1 = 28{\cdot}25$ dynes per cm. for benzene.

To displace air by water from the carbon required 12,000 grms./cm.^{2}; hence the wetting angle of carbon-water-air with $\sigma_2 = 72{\cdot}08$ dynes per cm. is 40° 35′.

Benzene was found to displace water from carbon with a pressure of 5,778 grms./cm.^{2}, giving with a value of $\sigma_{23} = 34{\cdot}65$ dynes per cm. an interfacial angle of 40° 30′.

CHAPTER II

THE SURFACE TENSION OF SOLUTIONS

1. The Gibbs Equation.

In the case of pure liquids the surface phase is naturally of the same composition as the bulk phase; for solutions, on the other hand, the composition of the surface phase need not necessarily be identical with that of the underlying solution. In general the addition of a solute to a solvent will affect the surface tension of the latter, and since the energy of the system strives towards a minimum there will be a tendency if the solute lowers the surface tension of the solvent for the former to accumulate at the surface. If the solute elevates the surface tension of the solvent, the reverse action occurs and the surface phase will be poorer in solute than the bulk phase. This enrichment or impoverishment of the surface phase does not continue indefinitely, for a point is reached when the action is balanced by the return from the enriched to the impoverished phase due to diffusion, the rate of which is proportional to the difference in osmotic pressures of the solute in the two phases.

The exact mathematical treatment for the calculation of the excess or deficiency of solute in the superficial phase was first made by Gibbs and independently a year later by J. J. Thomson, and Gibbs' equation may be regarded as the fundamental basis for the thermodynamical treatment of interfacial phases.

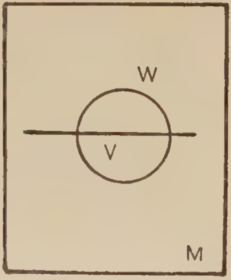
Gibbs' equation, which is perfectly general, may be deduced readily from the potential functions of Gibbs (*Thermodynamics*, p. 221) and Duhem (*Le Potential Thermodynamique*, Paris 1886), or in the following manner.

M is a vessel which encloses a system in equilibrium. W is a closed surface within the vessel which contains a volume V.

For any infinitesimal change in a reversible system, the change in energy may be written

$$dU = TdS - pdV + \mu_1 dm_1 + \mu_2 dm_2 + \dots \qquad \dots(1),$$

where S is the entropy, μ_1, μ_2 the chemical potentials of the components. This equation is true whether the matter within the surface W is homogeneous or not, so long as W does not intersect a phase boundary. When this condition is not fulfilled, a term of the form σdA must be added to the right-hand side of equation (1) for each interface intersected and also the second term will have to be resolved into parts if any of these interfaces are appreciably curved.



Let us consider the case in which there are two phases separated by an interface of which only an area A is within the surface W and in which the interface is flat. We obtain

$$dU = TdS - pdV + \sigma dA + \mu_1 dm_1 + \mu_2 dm_2 + \ldots \quad \ldots(2).$$

The non-homogeneous layer separating the phases is at least one molecule thick and may be thicker. Owing to lack of knowledge in this respect, it is convenient to imagine a geometrical surface drawn somewhere in this non-homogeneous region and parallel to it. This surface will divide the volume V into two parts V' and V'' which we may assign to each of the phases.

By assuming that the entropies S', S'' in ergs per c.c. per ° C. and the densities of each component ρ_1', ρ_2', ρ_1'', ρ_2'', etc. in mols. per c.c. which obtain in the bulk of the two phases remain constant right up to the dividing surface, we can assign a portion of dU to each of the phases

$$dU' = Td(V'S') - pdV' + \mu_1 d(V'\rho_1') + \mu_2 d(V'\rho_2') + \text{etc.},$$
$$dU'' = Td(V''S'') - pdV'' + \mu_1 d(V''\rho_1'') + \mu_2 d(V''\rho_2'') + \text{etc.},$$

p having the same value in both phases if the interface dividing them is flat. To the sum of dU' and dU'' must however be added a third term dU_i relating to the interface. Thus

$$dU = dU' + dU'' + dU_i.$$

In a similar way an increment of entropy and quantities of components must be present in the interface

$$dS = d(V'S') + d(V''S'') + d(AS_i),$$
$$dm_1 = d(V'\rho_1') + d(V''\rho_2'') + d(A\Gamma_1),$$

where Γ_1 is the surface concentration of one component.

Whence it follows that

$$dU_i = Td\,(AS_i) + \sigma dA + \mu_1 d\,(A\Gamma_1) + \mu_2 d\,(A\Gamma_2) + \dots \dots (3).$$

Let us now consider the energy required to increase the surface from an area A_0 to an area A.

The mechanical work required is $\sigma\,(A - A_0)$.

The heat required is $T\,(A - A_0)\,S_i$.

The chemical energy required is

$$\mu_1\,(A - A_0)\,\Gamma_1 + \mu_2\,(A - A_0)\,\Gamma_2.$$

This last term is necessary since the amounts of the various components required to make up the surface concentration of the newly formed surface cannot be taken from the bulk phases inside the surface W without altering the μ values of the components. They must therefore be introduced from outside the system and the intrinsic energy associated with them must be added to the system. We thus obtain

$$U_i - U_{i_0} = \sigma\,(A - A_0) + T\,(A - A_0)\,S_i + \mu_1\,(A - A_0)\,\Gamma_1 + \mu_2\,(A - A_0)\,\Gamma_2 + \dots.$$

On differentiation we obtain

$$dU_i = \sigma dA + A d\sigma + Td\,(AS_i) + AS_i dT + \mu_1 dA\Gamma_1 + A\Gamma_1 d\mu_1 + \mu_2 dA\Gamma_2 + A\Gamma_2 d\mu_2 + \dots \dots (4).$$

Subtracting from (3) and dividing through by A, we obtain

$$d\sigma = -\,S_i dT - \Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 - \dots.$$

For a binary system at constant temperature this reduces to

$$d\sigma = -\,\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2.$$

If our geometrical surface, which we have placed arbitrarily in the non-homogeneous region, be drawn in such a position that Γ_1 is zero, we obtain

$$d\sigma = -\,\Gamma_2 d\mu_2.$$

For ideal solutions the relationship between the chemical potential and the concentration is given by the expression

$$\mu = \mu_0 + RT \log_e c,$$

whence $-\,d\sigma = RT\,.\,\Gamma\,.\,d\log_e c$ or $\Gamma = -\dfrac{d\sigma}{RTd\log_e c}$.

For all non-ideal and concentrated solutions the concentration may be replaced by the thermodynamic concentration or "activity" fc defined by

$$\mu = \mu_0 + RT \log_e fc,$$

whence

$$\Gamma = -\frac{d\sigma}{RTd \log_e fc}.$$

The Gibbs equation may be expressed in other forms such as

$$\Gamma = -\frac{d\sigma}{RTd \log_e P},$$

where P is the vapour pressure of the solute, or

$$\log_e fc = -\frac{1}{RT}\int \frac{d\sigma}{\Gamma}.$$

It is evident that the unit of concentration is immaterial, but that if R be given the value $1{\cdot}98J = 4{\cdot}316 \times 10^7$ ergs/degree, Γ will be expressed in grm. mols per sq. cm.

The quantity of solute Γ transferred from the interior to the surface may be called the adsorption per unit surface. It may be positive or negative according to whether the solute lowers or raises the surface tension of the solution. Gibbs' equation shows us that whenever we have two components present in a liquid whose surface tension would be increased by an increase in the concentration of one of them, that constituent must have a lower concentration relative to the other in the surface than in the homogeneous phase. The field covered by the theorem is very wide, for it applies not only to all solutions commonly so called, but to associated or dissociated liquids and to substances capable of undergoing isomeric or tautomeric or allotropic change in the liquid state. Every such binary liquid is bounded by a surface film characterised not only by possessing a certain energy but also by its composition.

2. **The experimental verification of Gibbs' theorem.** Since the osmotic pressure of a solution is generally difficult to measure, it is simplest to choose a case such that Raoult's law holds good and the concentration of the solution may be used in place of osmotic pressure. The solution should therefore be dilute and should be a true solution: the solute, that is, must be dispersed as simple molecules and not as molecular aggregates like soap micelles. These conditions were obtained by Donnan and Barker

(*Proc. Roy. Soc.* A, LXXXV. 557, 1911), who employed a solution of nonylic acid. Their method of determining Γ was ingenious. A slow stream of air-bubbles was blown up through the solution, and the number and diameter of the bubbles were determined. Adsorption of solute occurred at the surface of each bubble, and the quantity so adsorbed was carried with the bubble into an upper part of the experimental vessel. Diffusion of solute back into the lower portion of the vessel was prevented by suitable baffles and the upper part gradually increased in concentration. If n was the number and r the radius of the bubbles, v the volume of the upper compartment of the vessel in c.c.s and Δc the concentration change in gram-molecules per cubic centimetre,

$$\Gamma = \frac{v\Delta c}{n \times 4\pi r^2} \text{ grm. mols per cm.}^2.$$

The change of concentration in any experiment was exceedingly small and was calculated by determining the surface tension before and after and comparing the results with a previously determined σ, c curve. Since a large change of surface tension is produced by a very small change in concentration, this is here a very delicate method of quantitative analysis. The following results were obtained:

C (molarity $\times 10^7$)	Γ observed mols/cm.^{2} $\times 10^{10}$	Γ calculated from Gibbs' equation
1·54	6·0	3·5
3·16	9·6	7·2
4·80	6·9	8·0
5·09	5·8	—

A similar experiment with solutions of saponine gave observed values of Γ about three times those calculated from the formula, but the concentration of saponine in true solution is probably very difficult to measure.

Similar experiments by Harkins and Gans (*Coll. Symp. Monograph*, V. 40, 1927; VI. 36, 1928) with nonylic acid and amyl alcohol yielded results of the same order of agreement.

McLewis (*Phil. Mag.* 1908, 1909) and Patrick measured the adsorption of mercuric nitrate, salicylic acid, picric acid, neofuchsin, aniline and caffeine at paraffin water, mercury water and interfaces. Of these cases only the two latter gave results in approximate agreement with Gibbs' theorem: every other substance showed an adsorption considerably too great, up to one hundred times the calculated value. We shall see, however (Ch. VII), that the extent of adsorption at a metal-liquid interface is dependent on the potential difference between the two phases and that when the change in thermodynamic potential due to the change in potential difference is taken into consideration, Gibbs' equation has been shown to hold by Schofield (see p. 309) for the adsorption of mercurous ions by an expanding mercury surface.

McBain and his co-workers (*J.A.C.S.* XLIX. 2230, 1927; LI. 3534, 1929) have examined the adsorption of a number of substances at an air liquid interface by an ingenious device for trapping a number of gas bubbles rising in an inclined tube. It is doubtful whether true equilibrium was ever reached in such a system, but it was found that, with the exception of nonylic acid, the amounts adsorbed in all other cases greatly exceeded those calculated with the aid of the Gibbs' equation expressed in the form $\Gamma = -\frac{d\sigma}{d\mu}$.

It is worth devoting some space to consider the causes of these deviations from the theoretical results of so fundamental a theorem.

We have referred already to the experiments of Schofield on the validity of the Gibbs equation for metal-solution interfaces when due consideration is paid to the interface potential, a factor neglected in earlier work. At air liquid interfaces there is another important phenomenon which has to be taken into consideration.

We shall have occasion to note (p. 63, p. 90 et seq.) that numerous substances can exist in the form of films at surfaces in well-defined states or phases; these films may be gaseous, vaporous, liquid, liquid crystalline, solid, bimolecular or colloidal. Of these all except the latter can exist as stable systems under specified conditions of temperature and concentrations.

For each surface phase the Gibbs law $\Gamma = -\frac{d\sigma}{d\mu}$ is valid, but it is clear that the actual measurements of $\Delta\sigma$ and $\Delta\mu$ must be taken only over those ranges of bulk concentration with which one and only one surface phase is in equilibrium. Thus, if the surface phase be progressively vaporous and liquid over regions of increasing chemical potential of the solute $\mu_1 - \mu_2$, $\mu_2 - \mu_3$, respectively, the measurements of $\Delta\sigma$ and $\Delta\mu$ must be taken within these regions to give $\Gamma_1 = \frac{d\sigma_1}{d\mu_1}$ for the vaporous, $\Gamma_2 = \frac{d\sigma_2}{d\mu_2}$ for the liquid phases respectively. It is evident that when a surface transformation, e.g. vapour to liquid, is taking place, $d\sigma$ and $d\mu$ must both be equal to zero. Consequently, if the observations are taken over such a wide range of concentration so that a phase change takes place, i.e., measurements of $\Delta\mu$ are made over the region $\mu_1 - \mu_3$ and are not confined to the region $\mu_1 - \mu_2$ or $\mu_2 - \mu_3$, the value of $\Delta\sigma$ observed will be far less than that which would have taken place if no surface transformation had occurred, and the observed value of Γ will be in excess of that calculated neglecting such transformation. In addition we may observe that the conditions of equilibrium over the region of phase transformation are only attained extremely slowly, leading to an over-estimate of the value of $\Delta\mu$.

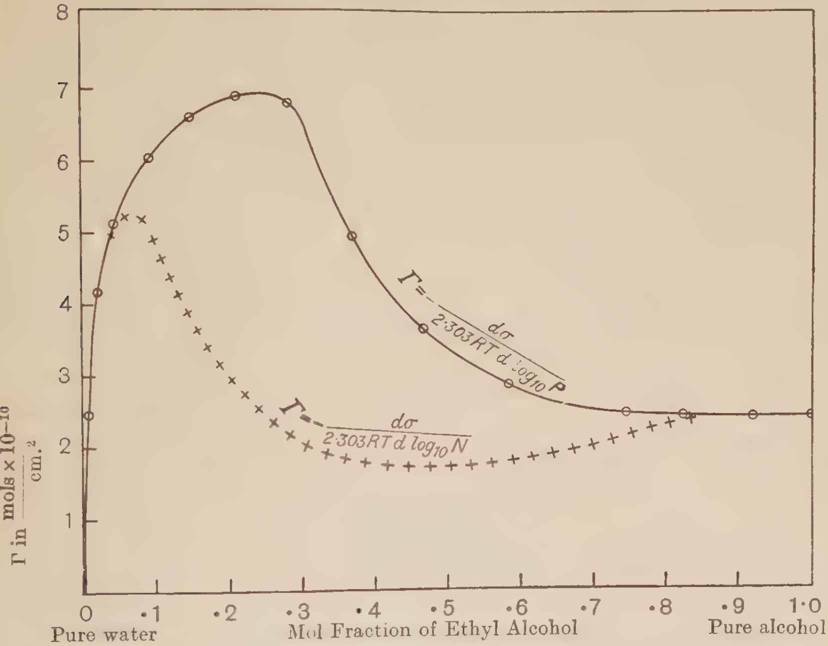
A somewhat different means of verifying Gibbs law has been attempted by Frumkin (*Zeit. physikal. Chem.* CXV. 499, 1925) utilising lauric acid. The surface saturation quantity (see Ch. III) was found to be $5{\cdot}2 \, . \, 10^{-10}$ grm. mols per sq. cm. Solutions of lauric acid were then made up in water and the surface tensions of these solutions determined; $\frac{d\sigma}{d \log c}$ was found to be 13·9, whence the surface adsorption is $\Gamma = -\frac{1}{RT}\frac{d\sigma}{d\log c} = 5{\cdot}7 \, . \, 10^{-10}$ grm. mols per sq. cm. The agreement is probably somewhat fortuitous, since the departure of solutions of long chain fatty acids from the laws of ideal solution commences at exceedingly low concentrations.

Although absolutely conclusive quantitative evidence for Gibbs' theorem is so far lacking, its qualitative truth is apparent from so many distinct sources that we may build upon it with considerable confidence, and in the remainder of this book it will be treated as a valid principle.

3. The surface tension of solutions.

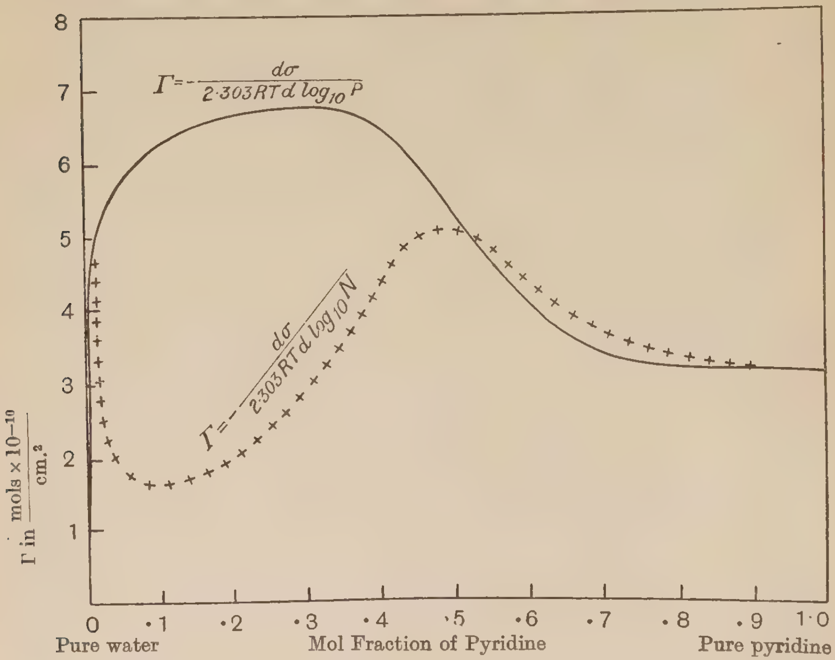
We might anticipate from a consideration of the Gibbs equation that the addition of a solute to a solvent will cause marked changes in the composition of the surface phase if the solvent and solute possess different surface tensions. On the addition of a highly capillary active material to water the surface phase becomes rich in the solute and the surface tension of the solution will fall rapidly.

Surface Excess of Ethyl Alcohol at a surface between air and mixtures of Ethyl Alcohol and Water.



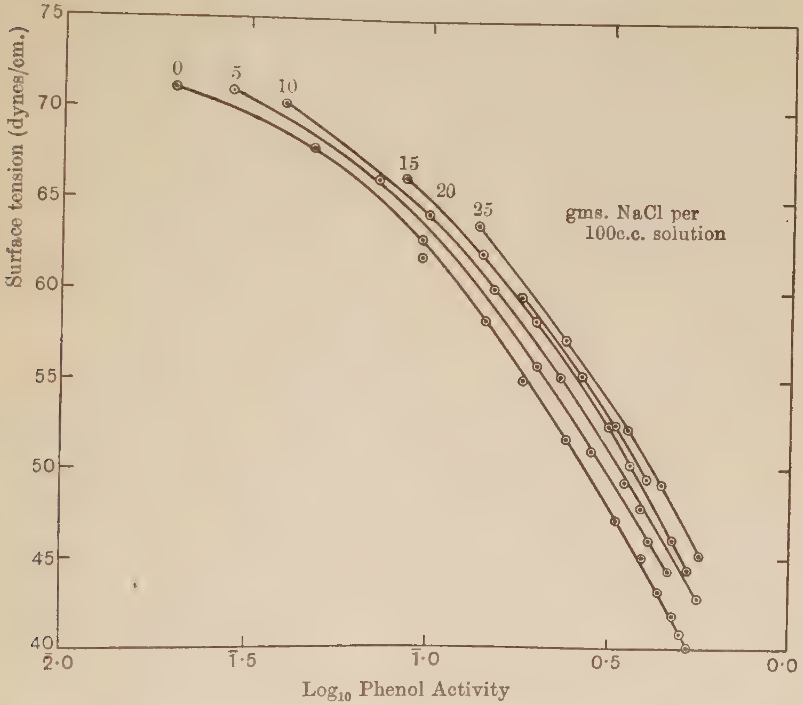
These conditions are realisable experimentally with solutions of the higher fatty acids and alcohols with water. The σ, N curve falls rapidly at first and subsequently approaches almost asymptotically a limiting value. With the aid of the Gibbs equation we may readily determine the form of the Γ, N curve, where Γ is the surface excess. The surface concentration may be assumed equal to Γ if we confine our attention to solutes of relatively high capillary activity. Again it is necessary to have information about the thermodynamic concentration or activity of the solute in the solution if the true value of Γ is to be determined.

Surface Excess of Pyridine at an interface between Mixtures of Pyridine and Water, and Mercury (no charge on surface).



For dilute solutions of non-ionising or feebly ionising solutes no serious error is introduced by employing bulk concentrations in lieu of activities, but in general serious errors are introduced through failure to take this precaution. The activities may be measured conveniently by means of any of the colligative properties of the solution, such as the partial vapour pressure, osmotic pressure or freezing point of the solution (see Lewis and Randall, *Thermodynamics*).

The data available for determining accurately Γ, *N* curves for such binary mixtures over a complete range of concentrations are limited, but the following examples are typical of the general form of these curves (Schofield and Rideal, *Proc. Roy. Soc.* A, CIX. 57, 1925). The two examples depicted in the curves are (1) ethyl alcohol water mixtures from the surface tension data of Bircumshaw (*J.C.S.* CXXI. 887, 1922) at 25° C. with the corresponding values of the partial vapour pressure of ethyl alcohol intrapolated from the data of Konovalow and Wrensky. By



means of the latter the values of $d\mu_2$ are obtainable with the aid of the equation

$$d\mu_2 = 2{\cdot}303RTd\log_{10}fc = 2{\cdot}303RTd\log_{10}P_2,$$

which is nearly exact for the small vapour pressures which these mixtures exert at 25° C. The Γ, N curve (where N is the mol fraction) is derived from the slope of the σ, $\log P_2$ curve by means of the Gibbs equation in the form

$$\Gamma_2 = -\frac{d\sigma}{2{\cdot}303RTd\log_{10}P_2}.$$

For comparison is inserted the Γ, N curve derived on the basis of ideal solution by the equation

$$\Gamma_2 = -\frac{d\sigma}{2{\cdot}303RTd\log_{10}N_2}.$$

It will be noted that there exist marked divergences between the two curves.

(2) The Γ, N curve for the adsorption of pyridine from an aqueous solution at a water-uncharged mercury interface. The surface tension measurements employed are those found by Gouy (*Ann. de Chimie et de Physique*, VIII. ix. 130, 1906), whilst the pyridine activities are derived from the vapour pressure data of Zadwiski extrapolated to 18° C. For comparison is inserted the Γ, N curve, regarding the pyridine water solution as ideal.

It is important to note that if the mercury surface be charged the extent of adsorption will be very materially affected (see Ch. VII). Lack of this precaution has vitiated the conclusions derived from a number of experiments, see ante, p. 51.

The σ, N curves for the surface tension of phenol in water, the activity of which can be varied by the addition of various concentrations of sodium chloride, present interesting features (*J.C.S.* CXXVII. 1668, 1925). The surface tensions were determined by the drop weight method, whilst the activities were obtained by a partition method utilising paraffin as parting liquid. The parting ratios were calibrated by means of freezing point determinations for pure phenol-water solutions by the method of Lewis and Randall. It will be noted that whilst the slopes of the curves for different salt concentrations are identical, indicating that for identical bulk activities of phenol the surface concentrations are likewise identical, yet the surface tensions are by no means dependent on the surface concentrations of the phenol alone even when this layer is tightly packed, but are affected by the nature of the underlying liquid. (From the value of Γ_∞ Å. is found to be 23·8 Å. for phenol on water, in close agreement with that obtained for vertically orientated substituted insoluble phenol derivatives by Adam.)

It will be observed that the Γ, N curves for such binary mixtures follow the same course—a rapid followed by a more gentle rise of Γ as N increases to a well-defined maximum followed by a drop and an asymptotic fall in the Γ value. In the case of alcohol water mixtures $\Gamma_{\text{max.}}$ is obtained at about $0{\cdot}3N$. To find an adequate explanation for the complete Γ, N curve is by no means an easy matter. It is clear that the first portion of the curve may be taken to represent an increasing surface concentration of alcohol and this proceeds to a limiting value—an observation first made by Milner (*Phil. Mag.* XIII. 96, 1907), who showed that for relatively strong solutions of acetic acid the surface tension of the solutions could be expressed as a function of the concentration of the acetic acid in the following form:

$$\sigma_0 - \sigma = \alpha + \beta \log_{10} N \quad \ldots\ldots\ldots\ldots\ldots\ldots(1),$$

where σ_0 is the surface tension of water, σ that of the solution, and α and β constants for the particular solute employed.

From (1) we obtain by differentiation

$$\frac{d\sigma}{d \log N} = -\beta,$$

and this equation together with that of Gibbs for ideal solutions,

$$\Gamma = -\frac{d\sigma}{2{\cdot}303RTd \log_{10} N},$$

leads to the expression

$$\Gamma = \frac{\beta}{2{\cdot}303RT}.$$

Similar conclusions as to the attainment of a finite maximum value of Γ as pointed out by Langmuir (*J.A.C.S.* XXXIX. 1883, 1917) can be obtained from an empiric equation put forward by v. Szyszkowski (*Zeit. physical Chem.* LXIV. 385, 1908) in the following form:

$$\frac{\sigma_0 - \sigma}{\sigma_0} = b \log_{10}\left(\frac{N}{N_0} + 1\right),$$

where b and N_0 are constants. If N be large compared with N_0, this equation approximates to that of Milner and we obtain likewise

$$\Gamma_{\text{limit}} = \frac{b}{2{\cdot}303RT\sigma_0},$$

also

$$\Gamma = \frac{bN}{RTN + N_0}.$$

An application of this relation to the data for ethyl alcohol would give a value of Γ corresponding to the maximum of the dotted curve which is evidently not the true maximum. Yet the idea that the excess of solute calculated with the aid of Gibbs adsorptive equation is situated in the outermost layer of atoms which Milner put forward on the strength of the above relation is one which as we shall note in the next section has been reaffirmed by Langmuir. Liquids which mix in all proportions and whose surface tensions in the pure state do not differ greatly frequently give Γ, N curves which are nearly straight. In some cases, such as in mixtures of carbon disulphide and dichlorethane, the addition of one liquid to the other produces a lowering of the surface tensions; thus on a carbon disulphide rich bulk phase dichlorethane is positively adsorbed and vice versa, the σ, N curve thus going through a minimum (at *ca.* equimolecular proportions, Whatmough). For the inorganic salts dissolved in water and alcohol the surface tension is raised, the surface phase is richer in water than the bulk phase and the increase in surface tension thus produced is nearly proportional to the salt concentration.

In rare cases—such as sulphuric acid and water—a surface tension maximum mixture is obtained (44 % H_2SO_2, Morgan).

Limitations imposed by the limits of mutual solubility of the liquids in the bulk phase in general, however, preclude examination of the σ, N curves over a wide range of concentrations.

We have noted that the Gibbs equation permits us to calculate the composition of the surface phase from a knowledge of the σ, N curve and the "activity" of the solute in the solution; it does not however give us any information as to the thickness of the phase, beyond an indication that the liquid above the geometrical dividing surface is uniform in composition and does not acquire the characteristics of a phase in bulk. In the next chapter our attention will be devoted to the behaviour of films of insoluble substances on the surfaces of liquids, and we shall have occasion to observe that we possess almost conclusive evidence that the surface phases of such films are but one molecule thick, and further that the molecules of the insoluble material adsorbed on the liquid are orientated in a vertical plane, being attached to the liquid surface in the case of a complex molecule by some particular group or groups.

These conclusions indicate that the Gibbs film, for such systems at any rate, is but one molecule thick, and it is evidently important to consider how far we are justified in making the assumption that in all cases both for pure liquids and for solutions the Gibbs layer may be considered as similar in character, viz. unimolecular in thickness and consisting of orientated or partially orientated molecules.

It has already been observed in the case of pure liquids such as substituted hydrocarbons that the surface tension was, if not completely defined by the non-polar portions of the molecule, at least not so markedly affected by substituent groups as we should anticipate if no orientation existed. Again, although vaporisation and condensation at a liquid surface such as water at high temperatures takes place with great speed, yet the life of a molecule on the surface is probably long enough to permit of such adjustment as orientation requires. Even more conclusive in favour of the hypothesis of at least partial orientation is the evidence derived from a consideration of the latent heats of evaporation and the divergences noted in the Eötvös constant for unsymmetrical undissociated molecules.

For mixtures of substances of markedly different surface tensions also we have noted that over a considerable range of concentration the Gibbs film appears to behave as if it were unimolecular in character, but for strong solutions of these substances as well as for mixtures of liquids of similar surface activities the evidence for such a restricted film thickness is by no means so conclusive. It must indeed rather be assumed that in these cases the application of the principle of minimum surface energy to mixtures somewhat similar in internal pressure leads to the formation of a diffuse layer in which the composition varies possibly in an exponential manner with the depth. The top layer alone may be said to be formed by the operation of chemical forces.

Thus in the case of concentrated solutions of ethyl alcohol in water the subsequent decrease in Γ with increasing values of N might, on the assumption of an orientated layer of alcohol molecules in the Gibbs film, be accounted for by a decrease in orientation when the more polar and presumably stronger water in the bulk phase is replaced by the weaker alcohol. Alternatively however the fall in Γ need not necessarily involve a rearrangement in the outermost layer of molecules. This is shown by the following considerations: in applying the Gibbs equation we have drawn our arbitrary dividing surface in such a position that the solution below it is uniform in composition as a whole. If we were to keep the position of the dividing surface fixed and at a depth of one molecular layer, the generalised equation

$$d\sigma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2$$

is applicable.

Since in a binary mixture $N_1 d \log f_1 c_1 + N_2 d \log f_2 c_2 = 0$, where N_1 and N_2 are the molar fractions of solvent and solute, we obtain from the above

$$-\frac{d\sigma}{RT\, d \log f_1 c_1} = \Gamma_1 - \Gamma_2 \frac{N_1}{N_2}.$$

With the aid of this equation only, which is applicable to all strong solutions, it is evidently not possible to determine both Γ_1 and Γ_2, the surface adsorptions of both solute and solvent; some other measurable property of the surface dependent upon its composition must be employed. Bradley (*Phil. Mag.* (7), VII. 142, 1929) has suggested that the alteration in the air liquid potential difference (see Ch. VII), which is dependent on the electric moments of solvent and solute molecules in the surface layers, may be used for this purpose. As we shall have occasion to note, the evidence for the assumption that the molecular electric moment of a molecule in the Gibbs layer at an air-liquid interface is independent of the surface concentration is by no means conclusive, and until further information is available it is a difficult matter to draw any conclusions as to the nature of the Gibbs film from information provided by the second portion of the Γ, N curve. But the fact that the change in surface tension from $N = 0{\cdot}3$ to $N = 1$ is only 6·0 dynes per cm. as against 44 dynes per cm. for the rest, tends to support a theory which does not involve any fundamental rearrangement of the *surface* layer in this region.

For the initial portion of the curve however we may conclude with some degree of assurance that the Gibbs film may attain a finite saturation value for the solute and does not become progressively thicker on increasing the concentration in the bulk phase.

4. The Unimolecular Gibbs Layer.

Langmuir from his study of the films of insoluble substances upon water (see Ch. III) concluded that the film was in these cases but one molecule thick and that the molecules in the film were definitely orientated.

He suggested that in all cases for both soluble and insoluble substances and for pure liquids the Gibbs film might be regarded as but one molecule thick and consist of pure solute molecules for substances which lower the surface tension of the solvent. If Γ be the surface concentration in grm. mols per sq. cm., on the hypothesis of a unimolecular layer of molecules we obtain $a = \frac{1}{\Gamma}$ as the area in sq. cms. per grm. mol or $\frac{1}{\Gamma N} = A$ as the area occupied by one molecule of the solute in the unimolecular Gibbs film.

In the following table are given the limiting values of A calculated from Milner's and v. Szyszkowski's equations by Langmuir and Harkins.

Acid. No. of carbon atoms in chain	Area in Å.^{2}
1	57
2	50
3	39
4	36
5	32
6	31
7	34
8	—
9	32
10	31

Langmuir considered these values to be "in substantial agreement with the value of A (25 Å.^{2}) found for insoluble films," though the discrepancy cannot be attributed to experimental error. Bury (*Phil. Mag.* IV. 980, 1927) has made an exhaustive study of the surface tensions and activities of butyric acid solutions, and by means of the equation $\Gamma = -\frac{1}{2{\cdot}303} RT \frac{d\sigma}{d \log fc}$ has determined the limiting areas at several interfaces with the following results:

	Å.^{2}
Water-air ...	32·0 at 25° C.
Water-benzene	33·8
Water-hexane	27·6

If we apply this hypothesis of the unimolecular character of the Gibbs film to our observed value of $\Gamma_{\text{max.}}$ for alcohol water mixtures, we obtain an area per molecule of 24 Å.^{2} as compared with a value of $A = 33$ Å.^{2} obtained with the aid of Milner's equation.

The application of the gas laws to surface films.

In the previous sections we have noted that the hypothesis of a unimolecular Gibbs layer for solutions of liquids of markedly different internal pressures together with the equation of Gibbs leads to values for molecular areas and thicknesses which are not at all unreasonably different from those determined by means of X-ray measurements, or from a study of insoluble substances on the surface of water, but cannot be said to be identical within the limits of experiment. In one respect, however, such soluble films differ from the insoluble films which we shall have occasion to examine in the next chapter; the surface tension of solutions, which according to the Gibbs adsorption equation

$$\Gamma = -\frac{N}{RT}\frac{d\sigma}{dN} \quad \text{......................(1)}$$

have a value of $\Gamma = 2 \,.\, 10^{-10}$ mols per sq. cm., give values of $\sigma_0 - \sigma$ which vary from 5 to 10 dynes per cm. at 20° C. The same number of molecules of palmitic acid put on a sq. cm. of water surface would not affect the surface tension of water by so much as one-tenth of a dyne.

Soluble substances appear to be capable of occupying enormous areas of the water surface and to be still capable of affecting the surface tension.

To explain this phenomenon Langmuir resuscitated a theory of Traube (*Lieb. Ann.* CCLXV. 27, 1891). The latter found that the quantity F, or the surface tension lowering, defined by

$$F = \sigma_0 - \sigma,$$

is approximately proportional to the bulk concentration for small values of F or

$$F = kN.$$

If the solution be regarded as ideal, this combined with (1) gives

$$F \cdot \frac{1}{\Gamma} = RT \quad \left(\text{since } \frac{d\sigma}{dN} = -\frac{dF}{dN} = -k\right)$$

or
$$FA = RT.$$

The resemblance between this equation and the equation $PV = RT$ for perfect gases led Traube to suggest that the lowering of the surface tension of a solvent by a solute is due to the thermal agitation of the solute molecules adsorbed at the surface. The observed surface tension is on this view the resultant of two forces, one the unaltered tension of the solvent σ_0 and the other an outward two-dimensional "gas" pressure exerted by the solute molecules in excess at the interface. According to Langmuir the failure of insoluble films to show this "gas" pressure is due to the considerable lateral attraction between hydrocarbon chains sufficiently long to cause insolubility, in consequence of which these films resemble liquids rather than gases. The possibility of the existence of films showing properties resembling the three states of matter had previously been suggested by Devaux (see Ch. III).

Langmuir adds that "surface liquids" may exert a "vapour pressure," though this is less than 0·5 dyne per cm. in all insoluble films so far investigated. We have noted that Traube's equation $F = kN$ does not obtain except for extremely small values of F, an observation which led Milner and v. Szyszkowski to develop the alternative empiric relationships between F and N already alluded to. If however we accept the hypothesis that we may apply a kinetic theory of surfaces for soluble substances in the unimolecular Gibbs film containing adsorbed solute molecules, it is clear that these adsorbed molecules can hardly be expected to behave like perfect gases where molecules are supposed to be infinitely small compared with the free space separating them. For at all but the smallest values of F the area per mol A is not much greater than the least area A_0 which a mol can occupy under high compression. It is therefore unreasonable to expect $\frac{FA}{RT}$ to be unity when $\frac{PV}{RT}$ for a real gas would not be. The values of $\frac{FA}{RT}$ over a range of values of F may, as shown by Schofield and Rideal (*Proc. Roy. Soc.* A, CIX. 58, 1925) conveniently be obtained by slightly transforming Gibbs' equation in the following manner.

Since
$$dF = \Gamma d\mu,$$
$$A = \frac{d\mu}{dF},$$

whence
$$\frac{FA}{RT} = \frac{d\mu}{RT}\frac{F}{dF} = \frac{d\mu}{2{\cdot}303RT}\,\frac{1}{d\log F}.$$

If the solution be ideal,
$$d\mu = 2{\cdot}303RT\,d\log_{10} c,$$

whence
$$\frac{FA}{RT} = \frac{d\log c}{d\log F}.$$

The data of v. Szyszkowski have been employed for determining the values of $\frac{FA}{RT}$* for butyric, valeric and caproic acids shown in the curves on p. 65.

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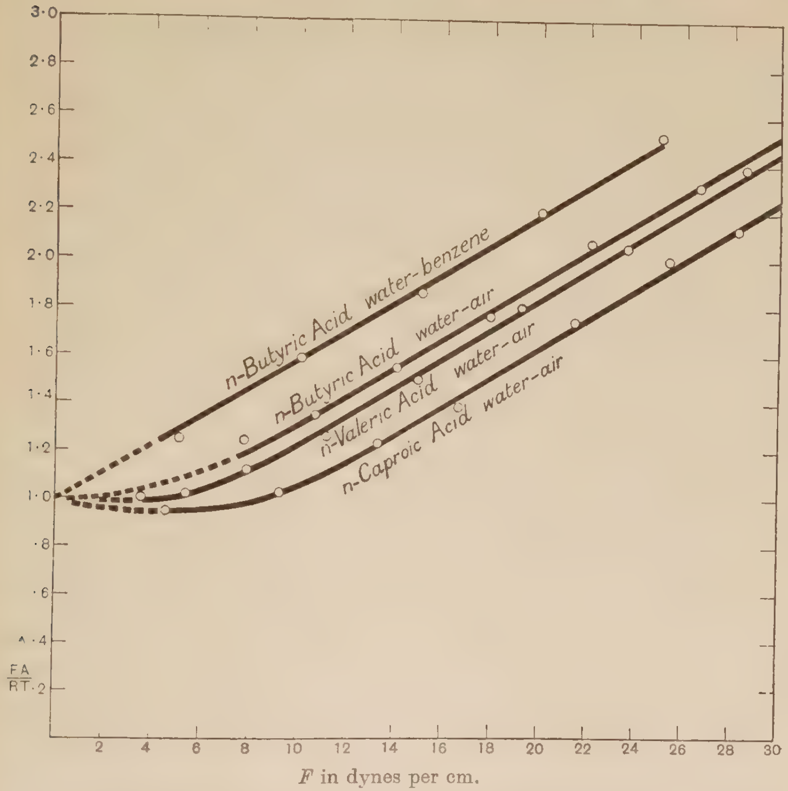
* For weak electrolytes the degree of dissociation found by the freezing point method agrees with that found from conductivity within the limits of experimental error, and Ostwald's dilution law is obeyed.

When the concentration c of a solution changes, the change in potential of the water is given by
$$d\mu_1 = -\frac{RT}{55{\cdot}51}\,d\,[c\,(1+\alpha)],$$
55·51 being the number of mols in 1000 grms. of water.

The corresponding change in the potential of the solute is
$$d\mu_2 = -\frac{N_1}{N_2}\,d\mu_1 = -\frac{55{\cdot}51}{c}\,d\mu_1 = RT\,\frac{d\,[c\,(1+\alpha)]}{c} = RT\left[\frac{dc}{c} + \frac{\alpha dc}{c} + d\alpha\right].$$

In the case of soluble substances of low capillary activity the evaluation of $F = \sigma_0 - \sigma$ is a matter of some difficulty, for this two-dimensional pressure must be regarded as the difference in surface tension between that of the liquid without the Gibbs film



Integrating this we obtain

$$\frac{\Delta\mu_2}{2{\cdot}303RT} = \Delta \log fc = \Delta \log c + \int_c^{c+\Delta c} a\, d\log c + \frac{\Delta a}{2{\cdot}303}.$$

The definite integral may be evaluated if a does not exceed 0·1 by means of Ostwald's dilution law $a^2c = K$. For $d \log c = -2d \log a = -\frac{2da}{2{\cdot}303}$. The last two terms which give the value of $\Delta \log f$ thus reduce to $-\frac{2\Delta a}{2{\cdot}303a} + \frac{\Delta a}{2{\cdot}303a} = -\frac{\Delta a}{2{\cdot}303a}$, whence $\Delta \log f = -0{\cdot}4343\Delta\sqrt{\frac{K}{c}}$. K for the higher fatty acids determined by conductivity measurements is $1{\cdot}5 \times 10^{-5}$.

and one in which the Gibbs film is established; only as a first approximation may the ideal dynamic surface tension of a solution, i.e. of a solution without a Gibbs film, be regarded as equal to the surface tension of the solvent.

The resemblance between these curves and the corresponding curves for a gas like nitrogen is most marked. The initial dip in the curve becomes more marked as the length of the hydrocarbon chain increases, whilst for large F values the slight negative curvature obtained for gases is faithfully reflected.

A consideration of the isothermals indicates that these two dimensional gases are by no means perfect and do not obey the Traube equation $FA = RT$ corresponding to the Boyle-Chasles law except at extremely low pressures. This departure from the ideal state has led to applications of modified equations of state.

Schofield and Rideal (*Proc. Roy. Soc.* A, CIX. 58, 1925) have employed the two-dimensional analogue of Amagat's equation

$$F(A - B) = iRT,$$

in which B is the limiting area, and $\frac{1}{i}$ is a measure of the lateral molecular cohesion, to represent the exact behaviour of surface films for all but the smallest values of F. The values of B and i for substances studied by v. Szyszkowski are given in the following table to which has been added the values for

Substance	Interface	B Å.^{2} per molecule	i	Observer
n-Butyric acid	Water-air	24·3	·73	v. Szyszkowski
n-Valeric acid	,,	24·3	·63	,,
n-Caproic acid	,,	24·3	·43	,,
Iso-butyric acid	,,	25·1	·78	,,
Iso-valeric acid	,,	25·1	·68	,,
Iso-caproic acid	,,	25·1	·48	,,
Iso-amyl alcohol	,,	—	·59	,,
n-Butyric acid	Water-benzene	24–25	1–·95	Harkins and King
Tertiary butyl alcohol ...	Water-mercury	24·0	·52	Gouy
Tertiary amyl alcohol ...	,,	28·0	·46	,,
Cane sugar ...	,,	72·7	1·0	,,
Pyridine ...	,,	26·0	1·0	,,

butyric acid at a water-benzene interface found from the measurements of Harkins and King (*J.A.C.S.* XLI. 986, 1919) and those for substances adsorbed at a water-mercury interface examined by Gouy.

All the normal acids show practically the same value of B at a water-air interface, a value which gives the mean area per molecule of $24{\cdot}3 \pm 0{\cdot}3$ Å.^{2} This value is also given by n-butyric acid at a water-benzene interface. The values of B for the iso-acids are consistently a little larger than those for the normal acids. The values of i show that these acids resemble gases whose critical temperatures increase as the carbon chain lengthens. The iso-acids have slightly larger values of i than the corresponding normal acids, indicating a decrease in the lateral cohesion between chains when branched.

It is interesting to note the large value of i for butyric acid at a water-benzene interface. Immersion of the hydrocarbon chains in benzene appears to decrease the attraction between the hydrocarbon chains.

This equation leads to a new relation between F and c, for, on eliminating A by means of the Gibbs equation, we obtain

$$\frac{\mu_2 - \mu_1}{2{\cdot}303RT} = i \log F + \frac{B}{2{\cdot}303RT} F,$$

or

$$\log fc = i \log F + \frac{B}{2{\cdot}303RT} F,$$

an equation which is found to give results which agree remarkably well with the precise surface tension measurements of v. Szyszkowski.

Volmer (*Zeit. physikal. Chem.* CXV. 255, 1925) has adopted the equation

$$F(A - B) = RT$$

and shown that it is obeyed for benzophenone, but does not give as is to be expected from the above data a good agreement with the observed values for any homologous series of organic compounds of the same type, whilst Bancroft (*J. Phys. Chem.* XXXI. 1501, 1927) without strong arguments in its favour suggests the form

$$FA = iRT.$$

We might also adopt a two-dimensional analogue of Van der

Waals' equation of state rather than any of those cited above; this is expressed in the form

$$\left(F - \frac{\alpha}{A^2}\right)(A - B) = RT.$$

(See Frumkin, *Zeit. physikal. Chem.* CXVI. 466, 1925; also Ch. VII, p. 306.)

It is evidently necessary to examine a number of F, A curves over a wide range of temperature to obtain sufficient data from which the various molecular constants can be deduced.

Adsorption of electrolytes.

In many cases such as at water-mercury interfaces electrolytes are positively adsorbed. The application of the kinetic theory to surface films of molecules leads, as we have seen, to a ready interpretation of the lowering of the surface tension by capillary active nonelectrolytes. For electrolytes an additional factor has to be considered, namely the mutual interaction of the electrically charged ions adsorbed. As we shall have occasion to note, the distribution of the adsorbed ions, both positive and negative, at an interface such as water-mercury is not readily determined, but it is clear from a consideration of the data of Gouy that mutual ionic electrical repulsion in the interface is an important factor. In the case of potassium iodide, for example, for very small values of F the Traube relationship

$$F = 2\Gamma RT$$

is obeyed (each molecule of KI yields two ions, thus the number of individuals in the surface phase is 2Γ). As F increases, instead of $\frac{FA}{RT}$ passing through a minimum, as is the case where molecules possess a certain lateral cohesion, the value of this quantity rises rapidly, indicating that a repulsive action of great magnitude is becoming operative as the superficial concentration increases. The nature and structure of this double layer so produced will be discussed in a later section.

Surface pressures.

In many cases the corresponding two-dimensional pressures for surface films may be evaluated by comparing the behaviour of a surface film with that of a gas or solution in the same condition, i.e. possessing the same value of i. Thus in the case of cane sugar ($i = 1$) the data of Gouy provide us with information on the surface tension of the interface water-mercury in the presence of varying concentrations of cane sugar, whilst we can, from the data of the Earl of Berkeley and Hartley on the osmotic pressure of cane sugar solutions ($i = 1$), evaluate the activity of such solutions with the aid of the equation

$$\frac{d\mu}{2{\cdot}303RT} = d \log \pi.$$

For an aqueous solution at 0° C. showing an osmotic pressure of one hundred atmospheres we find $\frac{\pi}{CRT} = 2{\cdot}3$, whilst $\frac{FA}{RT}$ has this value when the surface phase acquires an F value of 6·8 dynes per cm. (at 18° C.). It is evident that each dyne per cm. of F corresponds to nearly 14·7 atmospheres osmotic pressure, so that the "surface pressure" at a mercury interface, the surface tension of which has been lowered 30 dynes by cane sugar, is equivalent to an osmotic pressure of 440 atmospheres.

The ratio P/F is evidently equal to B/b when expressed in absolute units. Under high pressures at 0° C. the value of b for nitrogen is 30·5 c.c. per mol. n-butyric acid at a water-air interface may be compared to nitrogen at 0° C. between the pressures 400—1500 atmospheres, since $i = 0{\cdot}73$ for both substances. B for butyric acid $= 1{\cdot}49 \times 10^9$ sq. cm. per mol, hence

$$\frac{P}{F} = \frac{1{\cdot}49 \times 10^9}{30{\cdot}5} = 4{\cdot}82 \times 10^7.$$

Thus a surface pressure of one dyne per cm. is equivalent to a pressure of $4{\cdot}82 \times 10^7$ dynes per sq. cm. or 47·7 atmospheres.

The surface tension of solutions and chemical constitution.

Langmuir has pointed out that some important conclusions may be drawn from consideration of the surface and bulk concentrations of capillary active substances.

The diminution in potential energy of a molecular species when it passes from one phase in which it has a concentration c_1 to that of another phase of concentration c_2, with which it is in equilibrium, may probably be represented by an equation of the Boltzmann type

$$\frac{c_2}{c_1} = Ke^{-\frac{\phi}{kT}},$$

where ϕ is the decrease in potential energy accompanying the change. With this assumption a value of the relative polarity of different groups from a measure of the decrease in potential energy of the molecule as it passes from the interior to the surface phase may be obtained.

From a knowledge of the surface and bulk concentrations of various organic substances in dilute aqueous solutions, Langmuir has calculated the following values.

Group	Loss of potential energy in passing from the interior of the liquid to the surface, in calories per grm. mol
—CH_2— ...	710
Primary OH ...	570
Tertiary OH ...	950
Monobasic acids	473
Ester	470
Ketone... ...	295
Aldehyde ...	210
Amide	– 510
Primary amine	600
Dibasic acid ,, alcohol	– 700
Double bond ...	– 400
—OH in an acid	– 800

It is interesting to compare the values of ϕ thus determined for a series of solvents of varying internal pressure (cf. Hildebrand, *Solubility*, p. 116). The magnitude of the departures from Raoult's law of ideal solution vary in a manner which is highly significant as the ϕ values of solvent and solute diverge from one another.

We note also that each CH_2-group in a hydrocarbon chain is similar in character to each other, i.e. the loss of potential energy for a CH_2-group on passing to the surface is identical irrespective of its position in a chain.

From the partial vapour pressures of dilute aqueous solutions of the alcohols it is possible to determine the partition of the alcohol between the vapour and aqueous phase and hence for a homologous series of alcohols the change in potential energy occurring on taking a CH_2-group from the liquid to the vapour phase, this is found to be *ca.* 350 cals. (see Frumkin, *Zeit. physikal. Chem.* CXVI. 502, 1925). Since the loss in potential energy in taking the CH_2-group to the surface is 710 cals., we find that $710 - 350$ or 360 cals. must be expended in taking a CH_2-group from off the surface into the vapour phase, a quantitative expression for the assumption of Traube that the CH_2-groups are adhering to the surface.

Application of the Boltzmann equation to the distribution of a solute between the bulk and surface phases has been made by Langmuir (*J.A.C.S.* XXXIX. 1883, 1917), Herzfeld (*Zeit. physikal. Chem.* CVII. 74, 1923) and by Frumkin (*Zeit. physikal. Chem.* CIX. 41, 1924). A derivation of an adsorption isotherm may be made in the following manner.

If the thickness of the Gibbs layer be taken as δ and its area as A, when n_1 molecules are present in the layer, each of effective volume v, and n_2 molecules of solute are present in the solution of volume V, the free volume in the Gibbs layer left is evidently $A\delta - n_1 v$. If an additional Δn molecules be added to the solutions, a number Δn_1 will go into the surface layer and a number Δn_2 into the solution. On applying the Boltzmann equation we obtain

$$\frac{\Delta n_1}{\Delta n_2} = \frac{p_2}{p_1} \frac{A\delta - n_1 v}{V} e^{\frac{\phi}{kT}},$$

where p_2 and p_1 are the *a priori* probabilities of the molecules existing with potential energy ϕ and 0 respectively and may be taken each equal to unity.

Rewriting we obtain

$$\frac{\Delta n_1}{A\delta - n_1 v} = \frac{e^{\frac{\phi}{kT}}}{V} \Delta n_2.$$

Whence $n_1 v = A\delta - Ce^{-v\left(\frac{n_2}{V}\right)e^{\frac{\phi}{kT}}}$ on the assumption that ϕ remains constant (see, however, p. 315).

When $n_2 = 0$, n_1 must be zero also; hence

$$n_1 = \frac{A\delta}{v}\left(1 - e^{-v\left(\frac{n_2}{V}\right) e^{\frac{\phi}{kT}}}\right) = \frac{A\delta}{v}\left(1 - e^{-vc.e^{\frac{\phi}{kT}}}\right),$$

where c is the bulk concentration or

$$\Gamma = \frac{A\delta}{v}\left(1 - e^{-c.ve^{\frac{\phi}{kT}}}\right).$$

Whence we obtain at high concentrations $\Gamma_\infty = \frac{A\delta}{v}$, and Γ for small values of c is found equal to $A\delta\, ce^{\frac{\phi}{kT}}$.

From the Γ, c curves for dilute solutions at various temperatures the values of ϕ may be determined.

5. Negative Adsorption.

The inorganic salts raise the surface tension of water, and in accordance with the thermodynamic considerations implied in the Gibbs equation, the surface concentration of such solutions must be less than the bulk concentration.

Accurate experimental data on the subject of the surface tensions of such solutions are scanty. The values of Stocker for the dynamic tension by the method of the vibrating jet (*Zeit. physikal. Chem.* XCIV. 149, 1920), and of Harkins (*J.A.C.S.* XLVII. 2083, 1925) and Gilbert (*ibid.* XLVIII. 604, 1926), Goard (*J.C.S.* CXXVII. 2451, 1925) and Palitzsch (*Zeit. physikal. Chem.* CXXXVIII, 411, 1928) for the static tensions, may be taken as representative of the most accurate determinations in this field.

Over a considerable range of concentration for many salts the elevation in the surface tension is found to be approximately a linear function of the salt concentration or

$$\sigma_{\text{solution}} - \sigma_{\text{water}} = -F = Km,$$

where m = mols of salt per 1000 grms. of water.

A few of the values of K obtained by these observers for various salts are given in the table on p. 74. The values at 20° C. are taken from Goard and those at 25° C. from Harkins and Palitzsch.

In general the surface tension concentration curves are found to be slightly convex towards the concentration axis, a curvature becoming more pronounced for strong solutions. It is interesting to observe that with many salts of weak electrolytes the curves are initially concave to the concentration axis and that there occurs with increasing concentration a point of inflexion after which the convex type of curve obtained with the simple completely dissociated salts appears.

Such is found to be the case with both $CdCl_2$ and $AgNO_3$.

On the assumption of the unimolecular character of the Gibbs film we can, as Langmuir has indicated, obtain some idea as to the size of the solvent molecules. If the thickness of the film be δ and the bulk concentration C, the quantity of solute which has left the film, on the hypothesis of a unimolecular film of pure solvent existing at the surface, will be $C\delta$; this is equivalent to the negative surface excess or

$$C\delta = \Gamma = -\frac{d\sigma}{d\mu}.$$

The thickness of the adsorbed layer is thus $\dfrac{1000\,\dfrac{d\sigma}{d\mu}}{M}$.

Langmuir obtained a value of $\delta = 4$ Å. for the thickness of a water molecule in the surface of a solution of potassium chloride. From a knowledge of the molecular volume we obtain a cross-sectional area of *ca.* 7 Å.^{2} This calculation therefore involves a conception of an elongated water molecule whose diameter is about two-thirds of its length orientated vertically at the surface. Using Cederberg's values for the elevation of the surface tension of alcohol by dissolved salts (*J. Chem. Phys.* IX. 10, 1911), Langmuir obtains $\delta = 4{\cdot}4$ Å. and $A = 22$ Å.^{2}, a value in good agreement with that calculated by other methods, viz. 24 Å.^{2} (see *ante*). From a knowledge of the activity data of the salts, Harned (*J.A.C.S.* XLIV. 252, 1922), Goard (*loc. cit.*) and Harkins and McLaughlin (*ibid.* XLVII. 2083, 1925) calculated the values of Γ over an extended range of concentration and find that Γ is not independent of the concentration.

Salt	Mols per 1000 grms. water	K_{25}	K_{20}
NaCl	1·0	1·60	1·70
	2·0	1·61	1·71
	3·0	1·64	1·75
	3·22	—	1·82
	4·0	1·61	—
	5·0	1·63	—
	6·0	1·64	—
KCl	1·0	1·63	1·47
	2·0	1·53	1·52
	3·0	1·50	1·56
	3·8	—	1·60
	4·0	1·46	—
	4·8	1·44	—
LiCl	1·08	—	1·54
	1·94	—	1·62
	1·98	1·56	—
	2·53	1·62	1·81
	3·51	—	—
	3·76	1·67	—
	6·03	1·70	—
	10·0	1·62	—
	15·0	1·52	—
	20·0	1·40	—
NH_4Cl	2·0	1·24	—
	4·0	1·15	—
	6·0	1·12	—
	7·4	1·09	—
KBr	2·0	1·43	—
	4·0	1·36	—
	5·8	1·24	—
KI	2·0	0·95	—
	5·0	0·94	—
	8·0	0·94	—
	9·04	0·91	—
HCl	1·0	0·06	—
	5·0	0·13	—
	10·0	0·18	—
KNO_3	1·0	1·09	—
	3·0	0·99	—
	3·5	0·94	—
	3·8	0·92	—
$AgNO_3$	1·0	—	1·29
	2·0	—	1·07
	3·0	—	0·95
	5·0	—	0·92
$CaCl_2$	1·7	3·24	—
	4·0	3·69	—
	6·0	3·64	—
	7·3	3·52	—
$BaCl_2$	0·5	3·10	—
	1·0	3·14	—
	1·78	3·08	—
$CdCl_2$	0·47	—	2·04
	0·94	—	1·68
	2·36	—	1·57
	3·49	—	1·75
	4·71	—	1·91
$HgCl_2$	0·20	0·20	—
	0·27	1·08	—
Na_2SO_4	0·5	2·62	—
	1·0	2·48	—
K_2SO_4	0·5	2·74	—
$(NH_4)_2SO_4$	1·0	2·29	—
	3·0	2·24	—
	—	2·15	—
	5·0	2·23	—
	—	1·07	—
$MgSO_4$	1·0	1·99	—
	2·0	2·11	—
	3·0	2·55	—
$MnSO_4$	3·0	2·49	—
$KClO_3$	0·5	0·68	—
$KBrO_3$	0·3	1·67	—

The film thickness calculated from Γ would appear to vary with the concentration of the salt as indicated by the following data in which the negative adsorption in grm. mols per sq. cm. and the thickness of the layer δ in Å. are given.

Salt molarity	LiCl		NaCl		$CaCl_2$	KCl
	δ (Harkins)	δ (Goard)	δ (Harkins)	δ (Goard)	δ (Harkins)	δ (Goard)
0·1	3·54	5·5	3·54	6·0	4·4	4·0
0·2	—	5·25	—	5·75	—	4·2
0·5	3·3	4·25	3·4	4·7	4·0	4·4
1	2·4	3·2	3·2	3·75	3·8	3·85
2	—	2·3	—	3·05	—	3·25
3	2·0	2·1	2·6	2·7	2·6	2·95
4	—	—	2·35	2·55	—	2·75
5	—	—	2·30	2·45	—	—

The limiting values of δ are found to vary with the nature of the salt, the following data being obtained.

Salt	$\delta_{\text{min.}}$ in Å.
$CdCl_2$	3·9
$AgNO_3$	2·8
LiCl	2·0
NaCl	2·3
KCl	2·6

These values are much smaller than those calculated by Langmuir from somewhat scanty data and indicate that our conception of a layer of orientated solvent molecules existing at the surface must be modified.

It is interesting to note that the ionic mobilities lie in the order $\dot{K} > \dot{N}a > \dot{L}i$, whilst the true ionic radii are in the inverse order (Born, *Zeit. f. Physik.* I. 221, 1920). It is probable that the hydrated ions are always present in the surface but not necessarily in equal amounts, and that as the difference in concentration between surface and bulk phases increases this is accompanied by a simultaneous increase in the steepness of the concentration gradient from surface to bulk phase, a process which may be associated with the removal of water of solvation from around the ions.

Some further insight into the behaviour of salts at air-liquid interfaces may be obtained from a consideration of the electrification produced at such surfaces by solution of salts in the liquid, a point which will be considered in Ch. VII.

6. The adsorption of gases and vapours on liquid surfaces.

Iredale (*Phil. Mag.* XLV. 1094, 1923; XLVIII. 175, 1924) has studied the adsorption of a number of vapours at a mercury surface. The experimental data have led to a number of interesting conclusions.

The surface tension of mercury in the presence of the vapour at various partial pressures was measured by the drop weight method. The following values were obtained for the surface tensions of mercury in the presence of vapours of methyl acetate, water and benzene at various partial pressures at 26–27° C.

Methyl acetate		Water		Benzene	
Partial pressure mm.	σ	Partial pressure mm.	σ	Partial pressure mm.	σ
0	472	0	472	0	472
19	444	11·6	461	26·5	415
109	423	17·5	454	37·0	410
137	419	25	447–368	42·1	406
157	418			49·9	402
227	417			61·8	400
Sat.	412–370			76·3	396
				101·0	395–354

It will be noted that the fall in surface tension of the mercury with increase in the partial pressure of the vapour is similar to the fall observed in aqueous solutions with increase in concentration of a capillary active solute.

The vapours are evidently adsorbed on to the mercury surface and the amount adsorbed can be calculated with the aid of the Gibbs equation

$$\Gamma = -\frac{d\sigma}{d\mu},$$

where $d\mu = 2{\cdot}303\,RT\,d\log_{10} P$.

Calculating the maximum amount of each vapour adsorbed, we obtain for the limiting molecular area from the relationship $\Gamma = \frac{1}{A}$ the following values:

Vapour	Limiting area in Å.^{2}
Methyl acetate ...	27
Water	16
Benzene	21

which are in fair agreement with those calculated from the surface tension of solutions and indicate that in the adsorption of these vapours on mercury we are, in all probability, dealing with the formation of a unimolecular orientated adsorption film of vapour. In a similar manner Micheli (*Phil. Mag.* VII. 895, 1927) has measured by the drop-weight method the lowering of the surface tension of a water-air and mercury-air interface in the presence of the vapours of various hydrocarbons.

The limiting areas calculated with the aid of the Gibbs equation were found to be

Vapour	Water temperature (° C.)	Air interface	Vapour	Mercury interface
C_6H_6	25	40·8	C_6H_6	20·5
	40	56·05	C_5H_{12}	19·8
C_6H_{14}	25	17·9	C_6H_{14}	23·2
	35	24·9	C_7H_{16}	25·5
			C_8H_{18}	27·5

By determination of the partial pressures necessary for equal adsorption at two different temperatures the heat of adsorption of the vapours on the water surface were determined with the following results:

Vapour	Heat of adsorption cals. per grm. mol
C_6H_6	13,500
C_5H_{12}	13,600
C_6H_{14}	11,700
C_7H_{16}	14,600

These values for the adsorption of vapours are comparable with those obtained for the heat of adhesion or the heat liberated on bringing two liquid surfaces together, the method of measurement for which is described on p. 145.

Iredale (*Phil. Mag.* XLIX. 605, 1925) has extended his investigations on the adsorption of vapours at mercury surfaces by employment of the method of the sessile drop. He neglects any possible change in the angle of contact and employs the very approximate equation $H^2 = \frac{2\sigma}{g\rho}$. By this method he has obtained the following values for the limiting areas at the maximum adsorption:

Substance	Limiting area Å.^{2}
Methyl acetate	27·5
Benzene	21–23
Ethyl alcohol	29
Propyl chloride	about 40
Ethyl bromide	about 40

In the case of methyl iodide the adsorption was found to be associated with a large fall in surface tension of some 73 dynes per cm., and was also almost irreversible in that the surface tension did not rise again on reducing the partial pressure of the vapour. The limiting area of the stable surface compound was found to be quite small, being only some 13 Å.^{2}

It is further interesting to note that the transition from a primary adsorption film to a system in which the liquid is condensed on the mercury surface in the form of a thick layer, the free surface of which would possess the properties of the free surface of the liquid in bulk, is not abrupt. We observe that a point of instability is reached when the vapour pressure approaches saturation value and that the apparent surface tension of the drop can fluctuate within relatively wide limits. Iredale has shown that these values do not correspond to the tensions mercury/liquid, liquid/air, but may be due to a condensed film, a secondary film on the mercury surface. Whilst the transition from the primary film to the thick layer through the formation of secondary layers (Hardy, *Proc. Roy. Soc.* A, LXXXVIII. 316, 1913) takes place in this particular case within narrow limits of vapour pressure change, there is little doubt from the data that the change is definite although unstable, since the excess liquid above that necessary to form a unimolecular layer probably collects in minute droplets on the mercury surface. This continuous change in the P, σ curves obtained by Iredale near the critical point $P_{\text{sat.}}$ appears to be similar in character to the changes, observed by Goard and Rideal, occurring in the activity, σ curves for phenol water and salt mixtures near the salting out point, and may be taken as evidence for a progressive but not necessarily uniform thickening of the capillary layer before it acquires the properties of a bulk phase, a point to which we shall have occasion to refer.

Oliphant (*Phil. Mag.* VI. 422, 1928) has examined the selective adsorption of carbon dioxide admixed with either hydrogen or argon by a mercury surface. The method employed was an adaptation of that utilised by Schofield (see p. 309), in which the gaseous mixture entering at the centre of a vertical tube and flowing out at each end was submitted to analysis by a refractometric method. A stream of mercury drops falling down the tube enriched the gas flowing out at the bottom and impoverished that issuing from the top of the tube. He found that at all concentrations above about 2 % the carbon dioxide selectively adsorbed at the surface of the falling mercury was constant and of the order of $6{\cdot}5 \,.\, 10^{14}$ molecules per sq. cm. We may note that since the molecular diameter is some 4·2 Å., a close packed unimolecular layer would contain some $6{\cdot}0 \,.\, 10^{14}$ molecules per sq. cm.

Oliphant records the following data for the number of molecules per sq. cm. adsorbed from gases of different compositions at 16° C.

% CO_2 in H_2	Molecules per sq. cm. $\times 10^{-14}$	% CO_2 in argon	Molecules per sq. cm. $\times 10^{-14}$
0·5	3	5	6
2·0	5	10	6
5·0	7	15	5
10·0	7	—	—

The effect of pressure on adsorption of vapours.

In a manner analogous to that already given for the determination of the surface concentration in terms of the bulk concentration, we may find a relationship between the amount of vapour adsorbed on a liquid (or with certain assumptions on a solid) surface and the partial pressure of the vapour.

From the Gibbs equation $\Gamma = -\frac{d\sigma}{d\mu}$ we obtain $d\mu = -AdF$, and if the vapour be assumed to obey the perfect gas law we likewise obtain $-d\mu = v\,dp$, hence

$$v\,dp = AdF \quad \text{.......................(1).}$$

This equation can be combined with any of the four equations of the two-dimensional state given on pp. 66, 67 and 68.

Thus for very small adsorption the use of the Traube equation

$$FA = RT$$

is justified. From this equation we obtain by differentiation

$$FdA + AdF = 0,$$

whence $$dF = -\frac{FdA}{A} = -\frac{RTdA}{A^2},$$

and in a similar manner $dp = -\frac{RTdv}{v^2}$.

Inserting these in (1), we obtain

$$-\frac{RTdA}{A} = -\frac{RTdv}{v},$$

whence $$A = Kv = \frac{KRT}{p} \quad \text{or} \quad x = \frac{p}{KRT}.$$

The use of the Traube equation thus leads to a linear relationship between the amount adsorbed on the surface and the pressure of the gas or vapour.

At high pressures however we have seen that the Traube equation is not applicable, and the equation of Volmer $F(A - B) = RT$ or of Schofield and Rideal $F(A - B) = iRT$ must be employed, the former only in the case where the lateral adhesion between the adsorbed molecules is negligible. If it be assumed that the two-dimensional concentration be not too great so that $2AB > B^2$, then utilising Volmer's equation for the two-dimensional gas we obtain $x = \frac{p}{KRT + 2Bp}$ and we note that the surface would be saturated when $x_\infty = \frac{1}{2B}$ or only half completely covered, an assumption to be contrasted with the view of Langmuir (see p. 195).

We may also note that the rate of evaporation from the unimolecular film of adsorbed vapour may readily be calculated with the aid of the Herz-Knudsen equation. Thus in one of Iredale's experiments on adsorption of benzene vapour by mercury at a pressure of 12·5 mm. at 300° K. the value of $\frac{\Gamma}{\Gamma_\infty}$ calculated from the Gibbs equation gave a fraction of the surface 0·564 covered with benzene and a fraction 0·436 bare. The rate of condensation on the bare surface from the vapour is $0{\cdot}902 \,.\, 10^{-3}$ grm. mols per second, which is equal to the rate of evaporation from 0·564 cm.^{2} holding $0{\cdot}443 \,.\, 10^{-9}$ grm. mols. Thus the mean life of a benzene molecule on the mercury is $4{\cdot}9 \,.\, 10^{-7}$ seconds, comparable to $4{\cdot}7 \,.\, 10^{-8}$ seconds for a benzene molecule on liquid benzene at the same temperature.

Chemical reactions at gas-liquid interfaces.

A few cases of chemical reactions taking place at the gas-liquid interface have been noted. The process of skin formation in various protein solutions may be attributed to a reaction occurring at the phase boundary. The reduction in the enzyme activity of rennin investigated by Abderhalden (*Zeit. physikal. Chem.* LIV. 331, 1908), Schmidt Nielsen (*Zeit. physikal. Chem.* LXIV. 547, 1909) and Shaklee and Meltzer was shown by Rideal and Wolf (*Proc. Roy. Soc.* A, CVI. 98, 1924) to be due to a reaction taking place between rennin and a capillary-active dialysable material, probably a fatty acid at the air-liquid interface. The capillary-active constituent was found to be removable by selective adsorption on Fuller's earth or dry starch and could be displaced from the surface by capillary-active substances such as octyl alcohol or saponin.

Wu and Ling (*Chinese Journal of Physiology*, I. 407, 1927) have examined the coagulation of various proteins by shaking.

They find that whilst serum proteins and conalbumin are not changed by agitation, haemoglobin and egg-albumin are readily coagulated by this means. The coagulation was shown to be proportional to the air-liquid interface exposed and the rate found to be at a maximum at the isoelectric point of the protein, viz. P_H 9·8 for egg-albumin and 6·7 for oxy- and methaemoglobin; that in this case also the process of coagulation was taking place in a very thin layer is evident from the following data.

Amount of albumin coagulated per shake $= 3{\cdot}09 \,.\, 10^{-5}$ grm.

Area of effective surface during motion $= 70$ cm.^{2}.

Amount of albumin of density 1·3 coagulated per sq. cm. per shake $= 4{\cdot}4 \,.\, 10^{-7}$ grm.

$$\text{Thickness of layer} = \frac{4{\cdot}4 \,.\, 10^{-7}}{1{\cdot}3} = 34 \text{ Å}.$$

Whilst this thickness exceeds those obtained by Gorter and Grendel (see p. 116), it is in fair agreement with the value of 30·3 Å. obtained by Du Noüy (*Surface Equilibria of Biological and Organic Colloids*, p. 114. N.Y.). As in the case of rennin destruction the rate is decreased by the addition of capillary-active materials such as saponin and ether and increased by the addition of salts which raise the surface tension of water. No decision was arrived at as to the mechanism of the coagulation, but it appeared likely that the natural protein was first adsorbed at the air-liquid interface; it there underwent a process of denaturing followed by mechanical coagulation. In contrast to the view of Rideal and Wolf the protein was regarded as undergoing these changes without the presence of any other capillary-active material.

Harker and Neumann (*Proc. Roy. Soc. New South Wales*, LX. 45, 1926) observed that the rate of hydrolysis of isoamyl acetate at a hydrochloric acid interface was identical with the rate obtained at the surface when a mixture of water and ester-vapour is passed over it, the rate evidently being limited by the attainment of surface saturation.

CHAPTER III

THE SURFACE FILMS OF INSOLUBLE MATERIALS

1. Introduction.

Experiments commenced by Miss Pockels and extended by Lord Rayleigh (*Phil. Mag.* XLVIII. 331, 1899) indicated that a film of oleic acid spread on the surface of water continued to exert the same depressing action on the surface tension of the water until the thickness of the film, calculated from the area covered and the quantity of oil put on, was about 50 Å. In the neighbourhood of 20 Å. the tension was rapidly increasing as the film grew thinner until at 10 Å. it did not differ perceptibly from that of pure water. This thickness was known to be of the same order as the diameter of a molecule, and Rayleigh suggested that the thinnest oil films possibly consisted of only a single layer of molecules which could be regarded as floating objects.

Experiments on similar lines were carried out by Devaux (*Ann. Report Smithsonian Inst.* 261, 1913), Marcelin (*J. de Physique*, I. 19, 1914) and Labrouste (*Ann. de Phys.* XIV. 164, 1920). Meanwhile advances in other branches of molecular physics had led to very much more certain values for molecular dimensions, and when for triolein Devaux estimated the thickness of the thinnest film at 10 Å., while the mean molecular thickness calculated from the molecular volume and the Avogadro number was 11·3 Å., he concluded that this film was in fact only one molecule thick.

Devaux also advanced the important theory that the characteristics of the solid, liquid and gaseous states of matter are retained so long as one continuous layer of molecules remains unbroken.

The effect of temperature upon the properties of thin films was first investigated by Labrouste who showed that below a certain temperature the area of a continuous film of oil remained constant; as the temperature rises the area increases over a small range of temperatures usually some 15° C. and the area again becomes practically constant at a higher value.

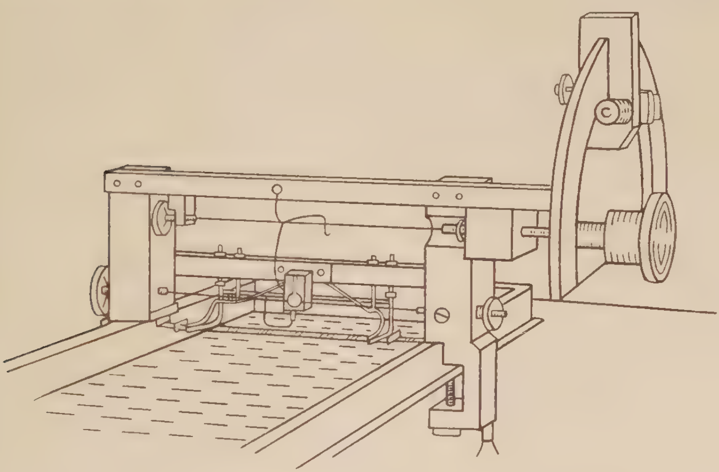
In 1917 Langmuir published his well-known paper on "The fundamental properties of liquids" (*J.A.C.S.* XXXIX. 1848, 1917; see also *Met. Chem. Eng.* XV. 468, 1916 and *Proc. Nat. Acad. Sci.* III. 251, 1917: in which his views were elaborated), in which he accepted the conclusion that films of oils on water were unimolecular and made further experiments on the subject by a direct method. This paper initiated the undertaking of experimental work on the subject of film formation by numerous investigators.

2. Experimental methods for examination of films.

(*a*) *The barrier methods.*

The surface tension of the films examined by Pockels and Rayleigh was determined by the force necessary to break them, a method open to some obvious objections, whilst the French investigators did not as a rule measure the tensions of the films but determined their maximum extension by scattering talc on the surface to make its boundaries visible and observing the maximum area which the film could be made to cover. Langmuir was the first to devise a differential apparatus which recorded simultaneously the area and the tensions of the films. The type of apparatus used with success by more recent investigators is essentially that of Langmuir, which with suitable modifications introduced by N. K. Adam is diagrammatically represented on p. 85.

It consists essentially of a shallow trough conveniently made of brass or nickel with parallel and smooth sides. Parallel to one end of the trough and suspended from a torsion wire by means of a fine silk suspension is a thin waxed copper strip, which is attached to the sides of the trough by means of thin platinum or gold leaf strips. This light copper strip thus acts as a movable barrier enclosing the film on the surface of water placed in the trough, escape of the film past the ends of the barrier being prevented by the strips of gold leaf. A waxed glass slide moved along the smooth sides of the trough parallel and towards the barrier permits of compression of the film, and the difference of tension between the water covered with the film and the clean water on the two sides of the movable waxed copper barrier can be compensated by a twist of the torsion wire. The torque of the wire is calibrated by hanging a small balance pan from an arm attached horizontally and at right angles to the centre of the wire and adjusting the torque for different weights placed in the pan. The whole trough is rigidly mounted on a firm base and levelled by suitable screw feet. With the aid of a mirror and by preserving a uniform temperature differential pressures as low as 0·1 dyne per cm. can be measured with some exactitude, and values as low as 0·01 dyne per cm. can be computed. Leakage of the film over the sides of the trough is prevented by a thin coating of pure wax.



To carry out an experiment the cleaned trough is filled with water and the surface scraped with a waxed slide to remove any accidental capillary-active impurities; a quantity of oil in dilute solution in pure redistilled benzene or petrol ether is dropped on the surface and the solvent allowed to evaporate. The area of the oiled surface is now altered by movement of the waxed slide with simultaneous measurement on the torsion wire of the differential tension required to maintain the floating copper barrier in its position of equilibrium; this differential tension is to be regarded rather as a two-dimensional pressure exerted on the film to keep it from spreading out indefinitely

$$\sigma_{\text{water}} - \sigma_{\text{oiled surface}} = F.$$

It is with this type of apparatus that almost all the quantitative work has been carried out.

(*b*) *Optical methods.*

There are two optical methods by means of which unimolecular films have been detected. The first, historically the earliest, is the only one by which the thickness of the film may be computed.

Jamin (*Ann. Chim.* XXXI. 165, 1851) noticed that when light plane polarised at 45° to the plane of incidence of the surface of a liquid was reflected at the Brewsterian angle the reflected beam was slightly elliptically polarised, the coefficient of ellipticity produced being dependent on the nature of the liquid. This coefficient measured by the ratio of the amplitude of the wave vector in the plane of incidence to that perpendicular to the plane was found to be positive for water and aqueous solutions and negative for most other liquids.

The cause for this ellipticity was first explained by Drude (*Theory of Optics*) on the classical electromagnetic theory by the assumption that instead of a sharp boundary between the two media there existed a thin film or layer over which a rapid transition took place; the ellipticity produced varies in origin according as the film is of greater refractive index than either medium or intermediate between the two. Drude's equation may be expressed in the form

$$\delta = \frac{K\lambda}{\pi} \frac{n_F^2 (n_1^2 - n_2^2)}{\sqrt{n_1^2 + n_2^2}\,(n_F^2 - n_1^2)\,(n_F^2 - n_2^2)},$$

where n_1, n_2, n_F are refractive indices of the media and the transition layer for light of wave length λ, and K the coefficient of ellipticity produced by a layer of thickness δ.

Drude thus established the cause of the ellipticity in the existence of a transition layer produced on reflection; he showed however (*Wied. Ann.* XXXVI, 532, 1889) that fresh cleavage surfaces of transparent crystals gave complete polarisation within the limits of his experiments. Rayleigh (*Phil. Mag.* (1), v. 33, 1892) concluded that Jamin's results were vitiated by contamination of the surfaces and on repetition of the experiments found that on clean water surfaces the ellipticity produced was either zero or very small, but on contamination of the surface with oil a noticeable change took place before even the camphor point was attained. He repeated these experiments on glass (*Phil. Mag.* (6), XVI. 444, 1908) and on diamond surfaces (*ibid.* 431, 623, 1912) and obtained an ellipticity which he states was probably due to contamination, and the possible existence of a unimolecular transition layer was definitely suspected. Fused quartz however gave no sign of a transition layer at the surface. Apart from contamination the ellipticity may be effected by a transition layer caused by an interpenetration of the two media (Wheeler, *Phil. Mag.* XXII. 229, 1911), or by a pressure on the reflecting surface (Volke, *Ann. d. Phys.* (3), XXXI. 609, 1910).

The Jamin-Rayleigh method of detecting thin films by observation of the change in ellipticity produced by reflection at a surface before and after a film had been placed on it has been employed by Ives and Johnsrud (*Proc. Opt. Soc.* XV. 374, 1927) to measure thin films of rubidium. Using a Babinet compensator instead of a quarter wave plate to determine the ellipticity, values of $\delta = 6$ Å. were detectable. Raman and Ramdas (*Phil. Mag.* (7), III. 220, 1927), using an apparatus similar to that of Rayleigh, measured the ellipticity produced at the surfaces of various liquids and showed that there was no noticeable relationship between the refractive index of the liquid and the ellipticity. On the arbitrary assumption that $n_F = \sqrt{n_2}$, they found that the thicknesses of the transition layers calculated with the aid of the Drude equation were of the order of molecular diameters as obtained from viscosity measurements. On covering a water surface with films of palmitic and oleic acids and assuming that $n_F = \frac{n_1 + n_2}{2}$ they obtained thicknesses for these films of $\delta = 13{\cdot}3$ Å. and $10{\cdot}0$ Å. for oleic and palmitic acids respectively. These authors concluded that the observed ellipticity at the surface of pure liquids was not due to an adsorbed film or to the orientation of the molecules, but due to the molecular motion causing a transition layer of optical density lower than the bulk density.

Frazer (*Phys. Rev.* XXXIII. 97, 1929), using an accurate photometric method for the determination of the ellipticity, has measured the values of K on the adsorption of the vapours of methyl alcohol and water vapour on glass. No detectable adsorption was observed with water vapour up to 2 mm. pressure, a gradual increase in condensation was noted over the region 6–12·5 mm., whilst at 13 mm. signs of strong condensation were observed. In the case of methyl alcohol condensation commenced at 30 % saturation, increasing until 90 % saturation was obtained when strong condensation set in. The thickness of a film of oleic acid on the glass surface was estimated to be 14·5 Å.

Bonhet (*C.R.* CLXXXV. 200, 1927) measured the ellipticities of polarised light for various salt solutions and showed that they were almost coincident with the value obtained with pure water, a result as we have seen in agreement with the hypothesis that the surfaces of solutions containing salts which raise the surface tension of water consist almost entirely of water. In the case of solutions of the fatty acids (*C.R.* CLXXXVIII. 59; CLXXXIX. 43), the ellipticity was found first to fall and then to rise with increasing concentrations, giving minimal values for the relatively insoluble ones at the point of saturation. In all cases a constant ellipticity was reached at the point where each molecule had an area of *ca.* 25 Å. on the surface.

Film formation on mercury surfaces has been examined notably by Sissingh and Haak (*Proc. Roy. Acad. Sci. Amst.* XXI. 678, 1919), Resser (*ibid.* XXIV. 102, 1921) and Ellerbroek (*Arch. néerland. Sci.* CXI. 10 A, 42, 1927), who showed that there existed gas films on mercury of the order of 16 Å. thick; an oil film was computed to be 30 Å. in thickness.

The second optical method for the examination of surface films involves the determination of the amount of light scattered by the surface. Gans (*Ann. d. Phys.* (3), LXXIV. 231, 1924; (3), LXXIX. 204, 1926) showed that on the assumption that the surface of a liquid was never quite plane owing to the thermal motion of the molecules constituting the surface, which motions were partly controlled by the surface tension of the liquid, light striking the surface at the critical angle would in general not suffer complete reflection but would suffer partial scattering. Gans investigated the case both for mercury and for transparent liquids.

Raman and Ramdas (*Proc. Roy. Soc.* A, CVIII. 561, 1925; A, CIX. 250, 1925) determined this surface scattering experimentally and showed that in general the observed scattering agreed with Gans' predictions. In agreement with the theory they found that the intensity of the scattering was greatest for liquids of high refractive index and low surface tensions. Later (*ibid.* A, CIX. 272, 1925) they observed that the surface scattering obtained with pure water was more than doubled by placing sufficient oleic acid on the surface to stop the motion of camphor and that the scattering increased enormously on the subsequent addition of more acid. In this case however photomicrographs revealed the presence of numerous minute lenses of oil whereas, before, the film appeared quite homogeneous. Molten palmitic acid behaved in a similar manner.

The surface scattering of liquid carbon dioxide was shown to increase considerably as the critical temperature was approached, and similarly the scattering at the interface between carbon disulphide and methyl alcohol increased on approaching the critical solution temperature; results in agreement with Gans' views as to the origin of the scattering for the interfacial tensions tend to vanish at this temperature.

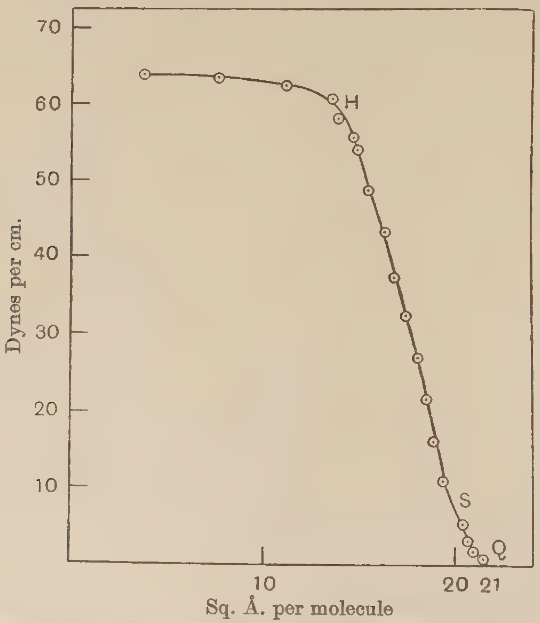
Finally we may note two other possible methods of investigation. According to Chella (*N. Cimento*, V. 416, 1928) the liquid films of oleic acid in the dark space of a Newton's ring series possess an absorption band different either from that of oleic acid or of water in bulk. Wolkowa and Titon (*Zeit. f. Phys.* LIII. 708, 1929; *Zeit. physikal. Chem.* B, IV. 71, 1929) passed a beam of parallel light through a cell half filled with liquid, the rays forming the image of the colimated slit passing half through the liquid and half through the air space just above the liquid; they noted that on momentarily disturbing the surface, two sets of interference fringes were observed which die away in the course of a few minutes. For aqueous salt solutions variation in the concentration of the dissolved salt was found to effect a linear deviation of the rays.

(*c*) *Measurement of the air-liquid potential difference.*

In addition to the use of the Langmuir trough and the optical methods which can be employed for the examination of surface films, we shall have occasion to describe the change in the air-liquid potential difference effected on placing a film-forming material on the surface of the water. The results obtained by this method, which are given in Ch. VII, are found to provide us with additional valuable information concerning the molecular architecture of the film.

3. Film structure.

As a typical example of the type of curve obtained with the aid of the Langmuir trough we shall take the case of palmitic acid on water at 16° C. The figure from Langmuir's paper shows the compressive force F (i.e. the difference, in dynes per cm., between the surface tension of pure water and of the oiled surface) plotted against the area occupied by one molecule measured in Ångström units.



At the lowest measurable compression (Q) the molecular area is 21·8 Å.^{2}, and the film is perfectly mobile, allowing floating particles of dirt to move about freely. On reducing the film area with the aid of the waxed slide, the compressive force rises following the curved line *QS*. The lowest part of this line appeared to be asymptotic to the axis of area. At *S* the dust particles on the surface lost their mobility as if now held rigidly in position. *S* is thus the melting point of the film. From *S* to *H* the line is practically straight and gives the compressibility of a two-dimensional solid. At *H* the film begins to crumple and strain lines may be observed on the surface similar to those of a collapsing saponin bubble. At this point the film as such ceases to exist.

At higher temperatures the melting point of the film occurs at higher compressions like ordinary solids which melt with increase in volume.

We have seen that earlier experimenters on the subject of thin films had reached the conclusion that these films were probably only one molecule in thickness. Rayleigh had suggested that at the point corresponding to *Q*, where the oil first exercises an appreciable effect on the surface tension of water, the film was one molecule thick; but that at the point *H*, where the maximum effect on the surface tension is reached, the film becomes bimolecular. Marcelin supported the theory of Rayleigh on the grounds of his own experiments with oleic acid in which the quantity of oil required to cover the surface at the minimum surface tension *Q* was one half that necessary at the maximum tension *H*. Devaux however pointed out that the ratio was not so great as two to one in any case, and explained the phenomenon by supposing the molecules to be capable of looser or tighter packing.

The theories offered so far gave no clue to the origin of the unimolecular films. Langmuir however pointed out that if the molecules in the film are regularly orientated on the surface of the water owing to the attraction between the water and the active groups of the organic liquid, these groups, e.g. $-COOH$, $-CH_2OH$, are dissolved as it were in water. The long hydrocarbon chains attached to them have no great tendency to dissolve, and thus stand up over the surface. "It is therefore evident," says Langmuir, "that there should be no particular reason for another layer of oil molecules to spread out on top of the first to form a second layer. In fact, since this upper portion consists exclusively of CH_3 or C_2H_5 groups, whilst in a globule of oleic acid, carboxyl groups are distributed through the mass, it is natural that the oil should prefer to remain in globule rather than to spread out as a layer two molecules deep. In the mass of liquid the carboxyl groups probably tend to gather into clusters because of the greater affinity of these groups for one another than for the hydrocarbon chains."

This conception of molecular orientation due to chemical forces at interfaces had already been suggested in somewhat more general terms by Sir W. Hardy (*Proc. Roy. Soc.* A, LXXXVI. 634, 1912; LXXXVIII. 303, 1913), who sought for the origin of these "directive" forces in the electrical structure of complex molecules. The following two quotations from Hardy's papers give an indication of the point of view.

"The corpuscular theory of matter traces all material forces to the attraction or repulsion of foci of strain of two opposite types. All systems of these foci which have been considered would possess an unsymmetrical stray field—equipotential surfaces would not be disposed about the system in concentric shells. If the stray field of a molecule, that is of a complex of these atomic systems, be unsymmetrical, the surface layer of fluids and solids, which are close-packed states of matter, must differ from the interior mass in the orientation of the axes of the fields with respect to the normal to the surface, and so form a skin on the surface of a pure substance having all the molecules oriented in the same way instead of purely in random ways. The result would be the polarisation of the surface, and the surface of two different fluids would attract or repel one another according to the sign of their surfaces." (1912.)

These ideas are even more clearly expressed in the following passage. "If the field of force about a molecule be not symmetrical, that is to say, if the equipotential surfaces do not form spheres about the centre of mass, the arrangement of the molecules of a pure fluid must be different at the surface from the purely random distribution which obtains on the average in the interior. The inwardly directed attractive force along the normal to the surface will orientate the molecules there. The surface film must therefore have a characteristic molecular architecture, and the condition of minimal potential involves two terms—one relating to the variation in density, the other to the orientation of the fields of force." (1913.)

Hardy thus bases the notion of molecular orientation at the surface on the existence of unsymmetrical fields of force surrounding the molecule; in other words, the parts of the molecule possessing the most powerful stray fields will be attracted inwards towards the bulk and thus cause a definite orientation of the whole molecule at the surface. More recent investigations on the variation in the air-liquid potential on placing a film at the interface confirm in great measure Hardy's views as to the lack of symmetry in the fields of force surrounding the molecules.

The theory of orientation of the molecules of fatty acids in thin films developed by Hardy and Langmuir received a brilliant confirmation in Langmuir's measurements of the limiting areas (at the point Q on the diagram) for molecules of various substances, all of which possess an "active group" such as —CO_2H or —CH_2OH, together with a long hydrocarbon chain. His results are given in the table. The lengths of molecules are obtained by dividing the cross-section into the volume per molecule calculated from the molecular volume and Millikan's value $6{\cdot}06 \times 10^{23}$ for the Avogadro number.

Substance	No. of C atoms	Cross-section Å.^{2}	$\sqrt{\text{Cross-section}}$ Å.	Length Å.	Length per C atom Å.
Palmitic acid	16	21	4·6	24·0	1·50
Stearic acid ...	18	22	4·7	25·0	1·39
Cerotic acid ...	26	25	5·0	31·0	1·20
Tristearin ...	57	66	8·1	25·0	1·32
Oleic acid ...	18	46	6·8	11·2	0·62
Triolein ...	57	126	11·2	13·0	0·69
Trielaidin ...	57	120	11·0	13·6	0·72
Myricyl alcohol	31	27	5·2	41·0	1·37

The table shows that many molecules are far from being symmetrical in shape, a direct confirmation of his theory. We notice incidentally the need for care in calculating the number of molecular layers contained in a thin film by the method of Rayleigh and Devaux, without further consideration. (If for example Devaux had chosen cerotic acid instead of triolein as his test case, he would have found 31 Å. as the thickness of the film, whereas the cube root of the volume of a molecule is $\sqrt[3]{31 \times 25} = 9{\cdot}2$ Å. Thus, neglecting the shape of the molecule, cerotic acid would have appeared to form a trimolecular layer.)

The cross-sections of the saturated acids do not vary much, but the length increases with the number of atoms in the carbon chain, as would be expected from Langmuir's theory. The alcohol has a somewhat greater cross-section than the acids. The cross-section of the glycerides is about three times as great as that of the acids from which they are derived, a fact easily explained on the supposition that the three acidic chains in each case lie side by side, occupying as much area on the water as if they were in separate acid molecules.

The case of oleic acid, which, with the same number of carbon atoms as stearic acid, occupies double the area on water, is of interest in that at room temperature this acid has already undergone the expansion noted by Labrouste. Thus films of long-chain acids can exist on the surface of water in at least three well-defined states—the solid condensed, the liquid condensed and the expanded states. We shall have occasion to note that in addition to these forms there exists in addition films in the highly attenuated or vapour state, thus presenting a series of states of attenuation until approximating to the gaseous state of the Gibbs layer of the short chain fatty acids discussed in the preceding chapter. We are indebted chiefly to N. K. Adam for a long series of careful measurements of the force/area curves of films of a number of materials in these various states, and both from the properties of the films themselves and from the nature of these force/area curves certain conclusions may be drawn as to the molecular architecture.

4. The condensed states.

If the force/area curve of an insoluble film-forming material, e.g. a hydrocarbon chain with a terminal polar group, be plotted at temperatures below the expansion temperature noted by

Labrouste, it is found that it consists in general, except at very low pressures, of two straight lines. In fig. 1 are shown the force/area curves for palmitic acid at ordinary temperatures on solutions of various acidities as determined by Langmuir (*J.A.C.S.* XXXIX. 1848, 1917), Adam (*Proc. Roy. Soc.* A, XCIX. 33, 1921) and Lyons and Rideal (*Proc. Roy. Soc.* A, CXXIV. 323, 1929). It will be noted that on solutions more acid than P_H 5 these two straight lines with intercepts at zero pressure of areas 20·6 Å.^{2} and 24·4 Å.^{2} respectively are clearly defined. As the underlying solution is rendered more alkaline, the low pressure and large area form of the film gradually disappears with decreasing limiting area until on relatively alkaline solutions only one straight line is obtained with the same limiting area of 20·6 Å.^{2} The film is found to be liquid in the low pressure large area region and solid in the high pressure region, whilst the "melting" of the film in as far as visual observation can decide occurs at the intersection of the two F, A curves.

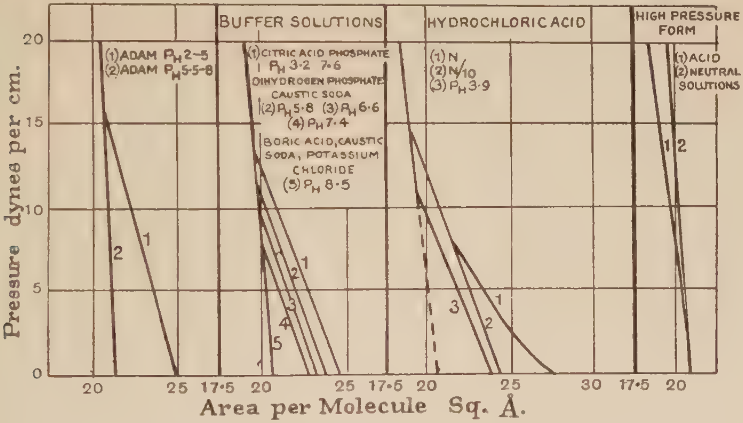


Fig. 1. The Force/Area Curves for Palmitic Acid.

The limiting area of 20·6 Å.^{2} (to 20·4 Å.^{2}) for the solid condensed film has been shown by Adam (*Proc. Roy. Soc.* A, CI. 452, 1922) to be characteristic of a number of substances consisting of hydrocarbon chains and different types of terminal polar or "head" groups, whilst the limiting area of the liquid condensed film varies not only as noted above in the case of the —COOH group with the reaction of the underlying liquid but also with the nature of the polar group. Whilst a systematic investigation similar to that given above for the —COOH group has not been made on the dependence of these limiting areas for the liquid condensed state on the nature of the underlying liquid, a few of these limiting areas, which as we have seen for acids is definitely characteristic of the —COOH group over a wide range of P_H, are given in the following table and are drawn chiefly from the very detailed and extended investigations of Adam.

Head group	Limiting area per molecule in liquid condensed form Å.^{2}	Reference
—COOH ...	24·4	
—NH_2 ...	30·6	
—OH... ...	21·0	Adam and Dyer*
—COOR ...	22·0	
—$OCOCH_3$ ...	23·0	
—phenol ...	23·8	Adam†
—anilin ...	23·7	,,
—CHBr COOH	27·2 but variable	Adam‡

* *Proc. Roy. Soc.* A, cvi. 645, 1924. † *Ibid.* A, ciii. 680, 1923.
‡ *Ibid.* A, ciii. 690, 1923.

(*a*) *The solid condensed state.*

The limiting area of 20·6 Å.^{2} for the solid condensed film is as we have noted characteristic of a number of substances consisting of hydrocarbon chains and different types of head groups, and from apparent agreement with X-ray measurements was taken as an indication that the film in this state consisted of vertically orientated close-packed molecules. The careful X-ray analysis of the structure of solid fatty acids by Müller (*Proc. Roy. Soc.* A, cxx. 437, 1928), Piper (*J.C.S.* 2310, 1926) and Thibault (*Trans. Farad. Soc.* xxv. 415, 1929) however has revealed that in such solid fatty acids the hydrocarbon chains are not in fact vertically orientated with respect to a plane through the carboxyl head groups, but are inclined to it at definite angles, in the more common crystalline form this angle being 63° 38′. Müller (*Proc. Roy. Soc.* A, cxiv. 542, 1927) suggested that a film in the solid condensed state might not in fact be vertically orientated but inclined in respect to the plane of the water surface. If the solid condensed film of numerous substances occupies but one characteristic area, some mechanism independent of the head group must be operative in restricting the inclination of the molecules, as is shown by the following analysis (Lyons and Rideal, *loc. cit.*).

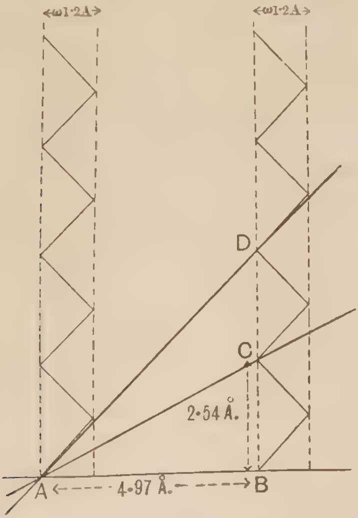
Two consecutive molecules in a molecular film of stearic acid are represented in the diagrammatical sketch.

The data for the unit cell, which contains four molecules, are given by Müller (*loc. cit.*) as $a = 5{\cdot}546$ Å., $b = 7{\cdot}381$ Å., $\beta = 63^\circ\ 38'$. From this we can calculate that the area occupied by two molecules perpendicular to the lengths of the molecule has the dimensions

$$a' = 5{\cdot}546 \sin 63^\circ\ 38' = 4{\cdot}97\ \text{Å.}, \quad b' = 7{\cdot}381\ \text{Å.}$$

Applying these results to the sketch below, we obtain

$$AB = 4{\cdot}97\ \text{Å.}\quad \text{and} \quad BC = 2{\cdot}54\ \text{Å.}$$



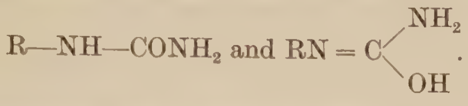
On calculation of the area occupied by one molecule, if it stands on the plane through BC and parallel to the b axis of the crystal (i.e. perpendicular to the plane of the paper), it is seen that $AC = (AB^2 + BC^2)^{\frac{1}{2}} = (2{\cdot}54^2 \times 4{\cdot}97^2)^{\frac{1}{2}} = 5{\cdot}58$ Å., which is in good agreement with the 5·546 Å. of the observed unit cell.

The area occupied by two molecules on this plane is $7{\cdot}381 \times 5{\cdot}58 = 41{\cdot}2$ Å.^{2}, and the area occupied by one molecule on this plane is therefore $20{\cdot}6$ Å.^{2}, which is in very good agreement with the actual area occupied by one molecule in a unimolecular film.

In other words, the molecule occupies on the surface of water the area it would occupy on a plane through AC, which is a plane such that relative to the neighbouring chain each chain has moved up a distance equal to two carbon atoms (one whole zig-zag).

There is thus only one stable position of tilt, which is identical for a large number of molecules with different head-groups. These head-groups are generally all small in size, so that they are unlikely to force the molecules farther apart from one another; although exceptions are found in cases where the molecules possess large head-groups, e.g. the α-bromocarboxylic acids. They are all asymmetric in character or asymmetrically attached to the chain. This asymmetry will give rise to a tendency of the molecule to tilt, and in practice tilting occurs such that one chain is moved up relative to the next by one whole zig-zag. This position will be of great stability, as the chains will then once more interlock with one another; for, although the chains are not in contact, their fields of force will vary in a zig-zag manner like the chains themselves. Thus every head-group which has sufficient asymmetry and adhesional force to cause the molecule to tilt at all, will cause it to tilt to this angle at which the chains again interlock, and it would need considerably more force to cause it to tilt to the next stable state, i.e. in the plane AD (fig. p. 97), in which each chain would have moved relative to its neighbour by a distance of four carbon atoms (two whole zig-zags).

Examples of molecules tilted two whole zig-zags of carbon atoms by very asymmetric heads, and thus presenting in the solid condensed film an area of 26·1 sq. Å. per molecule, are rare; Adam has shown that the long chain ureas give two types of stable and solid films in the high pressure less compressible form having areas at zero compression of 20·8 sq. Å. and 26·3 sq. Å. per molecule respectively (values obtained by extrapolation of Adam's curves), the form having the larger area being stable below a certain critical temperature. The areas obtained for these two forms agree well with those calculated, viz. 20·6 and 26·1 Å.^{2} respectively for molecules tilted in the two interlocking positions. The two forms may be ascribed to the different asymmetries of the isomeric forms of the urea head-groups



$$R\text{—}NH\text{—}CONH_2 \text{ and } RN=C\begin{matrix} \diagup NH_2 \\ \diagdown OH \end{matrix}.$$

It is possible that films of monomyristin and monopalmitin of areas 26·3 ± 0·5 sq. Å. which Adam describes as very viscous liquids and on which dust does not move very easily are in reality solids of weak rigidity.

(*b*) *The liquid condensed state.*

Films in the low pressure or liquid condensed state possess limiting areas which are dependent on the nature of the head-group and are regarded by Adam as possessing head-groups of different areas in contact with one another, whilst the less steep F, A curve obtained in this state is a measure of the compressibility of the head-group. We have noted however that the limiting area of palmitic acid is dependent on the acidity of the underlying solution. According to Adam's view, the packing of the head-groups must thus vary with the P_H of the solution. Langmuir (*loc. cit.*) attributed the increase in compressibility and area at low pressures on acid solutions to an increase in size of the head-group by adsorption of hydrogen ions from the underlying solution accompanied by an increase in mobility of the film, whilst Hartridge and Peters (*Proc. Roy. Soc.* A, CI. 348, 1922) and later Egner and Hägg (*Phil. Mag.* IV. 667, 1927) suggested that the two forms of the film corresponded to the non-ionised and ionised states of the head-group. We may note however that these two forms of film are obtained with substances for which a similar explanation is impossible.

It is possible that the liquid condensed film is in a smectic state, the two-dimensional analogue of the liquid crystalline condition. The chains of the molecules are to be regarded as no longer rigidly interlocked, and the limiting tilt observed corresponding to the limiting "head areas" of Adam results as the equilibrium position attained by the molecule under the directive forces of lateral adhesion of the chains and the directive attraction of the head-group for the underlying liquid.

These are given in the following table, the areas of the molecules in the liquid condensed state being:

Head group	Area per molecule in liquid condensed state Å.^{2}	Angle between long axis and valency direction of polar head
—COOH	24·4	137·5
—NH_2	30·6	127·0
—OH	21·0	149·0
—COOR	22·0	147·5
—$OCOCH_3$	23·0	144·0

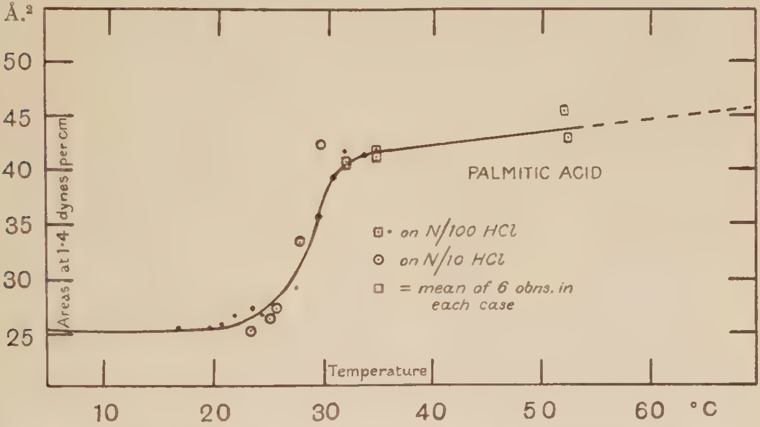
The angle which a terminal —CH_3 group makes with the long axis of the chain is, according to Müller (*loc. cit.*), from 129° to 136°. Thus both the —COOH and —NH_2 groups present the features of a relatively symmetrical terminal group, the terminal —OH being, as is to be anticipated, most unsymmetrical.

A change of state of a film may be produced by the formation of suitable mixed films. Leathes (*Zeit. f. Physiol. Chem.* CXXX. 113, 1923) noted that fatty acids on dilute hydrochloric acid under conditions where they would exist normally in the expanded state were converted into the condensed state on the addition of but small amounts of cholesterol which exists normally in the condensed state. Adam and Jessop (*Proc. Roy. Soc.* A, CXX. 473, 1928) have examined this phenomenon in more detail and have found that not only can expanded films of an acid such as myristic acid be converted into condensed films by such addition, but they showed that the surface vapour pressure of various substances would be reduced by the addition of cholesterol, which possesses no sensible surface vapour pressure, to an extent almost identical with the depression calculated with the aid of Raoult's law. A similar condensing effect was observed with other substances existing normally in the condensed state, such as tripalmitin and penta-erythritol tetrapalmitate.

5. Expanded Films.

Labrouste was the first to notice that below a definite temperature the area of a continuous film of oil remained constant, the area commencing to increase above this temperature until it becomes practically constant at a higher value. This change in area took place over a temperature range of about 18° C. This phenomenon has been investigated in detail by Adam, who has assigned the name of "expanded film" to the superficial phase in this state.

Adam has measured the increase in area obtained on elevation of the temperature under conditions of constant compression. A typical *A*, *T* curve under a pressure of 1·4 dynes per cm. is shown in the following diagram.



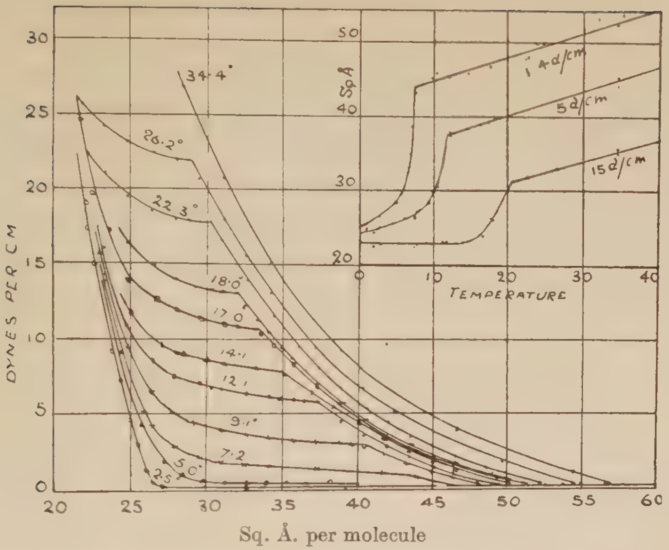
It will be noted that the existence of a temperature range of expansion *ca.* 13° C. is confirmed, the temperature of half expansion being in this case 28·5° C., whilst the area of the expanded film at this *F* value is *ca.* 41 Å.² Langmuir in his investigations on the areas occupied by fatty acid molecules on the surface of water obtained an area of 46 Å.² for oleic acid as compared with 21–25 Å.² for the saturated fatty acids, and imagined that the double bond in the unsaturated acid bent down to make contact with the water. In reality, as Adam showed, this is not the case, for oleic acid, at the temperatures at which Langmuir's investigations were carried out, forms an expanded film in which the area occupied is about twice that of the same acid in the condensed state.

The expansion temperature ranges for a number of substances at 1·4 dynes per cm. compression have been obtained by Adam with the following results.

Substance	Temperature of half expansion ° C.	Approximate area of expanded film corrected to 0° C. in Å.^{2}
Palmitic acid	28·5	36·8
Methyl palmitate	27·5	46
Ethyl ,, ...	13	55
Propyl ,, ...	< 5	76
n-Butyl ,, ...	< 5	74
n-Octyl ,, ...	< 5	76
Ethyl stearate...	33	45·4
Tripalmitin	48	29·5
Tristearin	57	29·9
Cetyl alcohol	49	30·8
Heptadecylurea	55	33
Stearic amide	58	32·2
Stearic nitrile	26	36·4
Octadecylamine hydrochloride	26·5	46
Stearic acid	46	36·1
Oleic acid	< 0	50·5
Lauric acid	< 0	45·1
Tridecylic acid	< 0	42·5
Myristic acid	9	40·6
Pentadecylic acid	19·5	38·8
Margaric acid	37·5	36·6

It will be noted that the expansion temperature for an acid increases with the length of the hydrocarbon chain (about 8° C. per CH_2), there being no difference between the odd and even numbers of the series as exists in the melting points of the crystals, whilst there is a progressive decrease in the apparent expansion area at 1·4 dynes compression for the acids as the chain increases.

Adam and Adam and Jessop (*loc. cit.*) have likewise examined the F, A curves for a substance such as myristic acid (temperature of half expansion under 1·4 dynes per cm. 9° C.) over both the region of condensed and that of expanded film. A few of the isotherms obtained for myristic acid are given in the diagram.



The pressure at which expansion commences is defined by the temperature to which the film is exposed, and above a certain critical temperature it is probable that the existence of a condensed film is impossible.

In the expanded state the limiting areas are clearly not great enough for the molecules to be lying flat on the water surface, thus for stearic acid in this state the limiting area even under very low compressions does not exceed 50 Å.², whilst for a molecular length of 21 Å. and cross-section of 5·2 Å. a horizontal molecule would occupy at least 109 Å.² of area. The molecules, if in the vaporous state, i.e. not in continuous contact with one another as originally suggested by Adam, cannot thus be lying down on the water, but must be inclined to the water surface with part of the hydrocarbon chain in the air. The assumption that expanded films are analogous to the three-dimensional liquid state rather than the vaporous has been advanced from several points of view. A film-forming material such as myristic in the expanded state does not expand rapidly and indefinitely (Cary and Rideal, *Proc. Roy. Soc.* A, CIX. 301, 1925) as the area of water over which the film could spread is suddenly increased. There appears in fact to be a limiting area beyond which "expansion" is relatively slow. From a study of the FA/F curves of expanded films (Schofield and Rideal, *Proc. Roy. Soc.* A, cx. 167, 1926), we may conclude that they behave as two-dimensional fluids above their critical pressures and thus as liquids. Langmuir (*Third Colloid Symp. Monog.* p. 48, 1925) likewise concludes that inclined molecules with part of the hydrocarbon chain in the air, a necessary feature of the vaporous state with these limiting areas, would be essentially unstable since the adhesion of the hydrocarbon —CH_2-groups both for one another and for water is by no means negligible (see p. 70). Consequently the molecules must be always partly enmeshed with one another in a state analogous to a three-dimensional liquid.

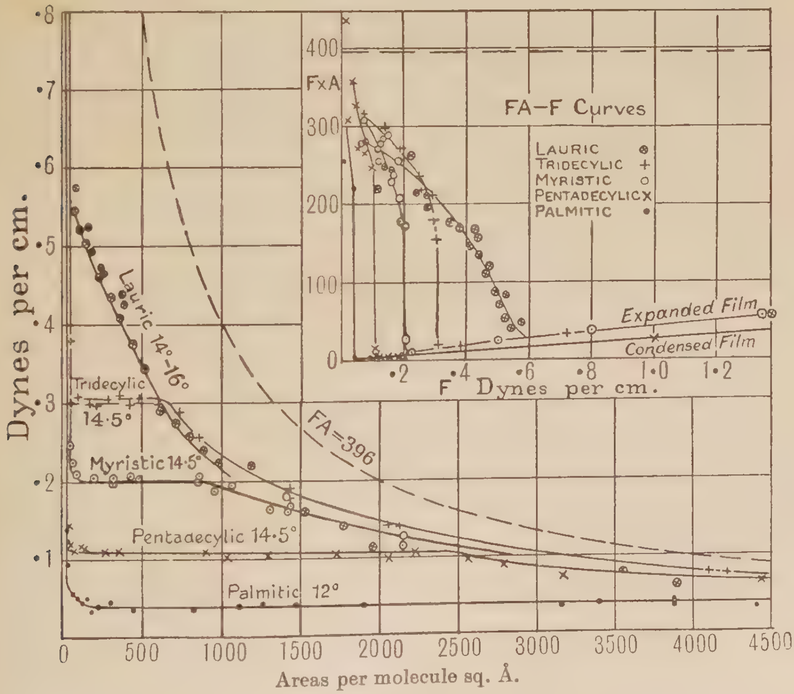
This suggestion as to the liquid nature of expanded films was finally confirmed by Adam and Jessop (*Proc. Roy. Soc.* A, cx. 423, 1926), who with a sensitive apparatus effected the measurement of the true pressure of the "vapour" in equilibrium with expanded films.

6. Vaporous Films.

In previous sections we noted that the behaviour of short chain fatty acids on the surface of water was similar to that which might be anticipated for the properties of two-dimensional but very imperfect gases. Since the van der Waals' adhesional term increases with the chain length, the transition at ordinary temperatures from the gaseous to the vaporous state, i.e. a lowering of the critical temperature, is easily effected by an increase in the chain length. We should anticipate that the conversion of the expanded liquid to vaporous films could be effected on sufficient decrease of pressure. Such vaporous films should evidently be even further removed from the perfect state where the Traube equation $FA = RT = 1{\cdot}372T$ (where F is measured in dynes, A in sq. Å. per grm. molecule) might be obeyed, than the gaseous films previously described.

Marcelin (*Ann. de Phys.* (4), x. 471, 1925) was the first to observe this fact and attempted to express the form of the F, A isotherm by the expression $FA = xT$, where $x < R$. Delaplace (*J. Phys. et Radium*, VI. 9. 111, 1928) has likewise measured the pressure area isothermal for surface solutions of benzoyl-benzoate from $F = 0{\cdot}10$ to $F = 0{\cdot}001$ dyne per cm. and has also expressed his results by the relationship $FA = xT$, where $x < R$. The presence of such vaporous films on decrease of pressure is likewise readily observed at the critical pressure, where during the change of state from two-dimensional liquid to vapour and *vice versa* at constant temperature the two-dimensional pressure should remain constant.

A few of the curves obtained by Adam and Jessop (*loc. cit.*) are shown below.



The critical phenomena for all the acids except lauric acid, which is above the critical point, are clearly marked in the diagram.

The change in free energy $F\,(A_1 - A_2)$ as well as the latent heat of two-dimensional vaporisation from the two-dimensional liquid expanded film may be determined from a knowledge of these critical data.

Adam and Jessop consider that $\frac{dF}{dT}$ is about 0·01 dyne per cm. per degree. For these acids they give the following values at 14·5° C.

Acid	Limiting area Å.^{2}	Vapour pressure dynes per cm.	Free energy change cals./grm. mol.	Latent heat of change cals./grm. mol.
Tridecylic acid	550	0·30	220	2000
Myristic acid	850	0·19	230	3200
Pentadecylic acid	2400	0·11	360	9500
Palmitic acid	—	0·004	—	—

Whilst the accurate determination of these critical data for such low pressures is admittedly a difficult matter, it will be observed that the data for the latent heat of change give values which are by no means small.

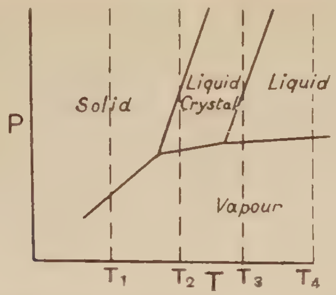
Guastalla (*C.R.* CLXXXIX. 241, 1929) has obtained similar results for oleic acid.

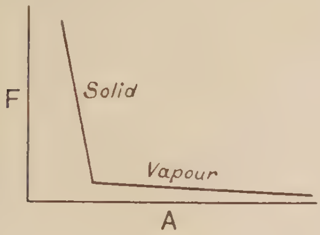
7. Factors influencing the transition of state.

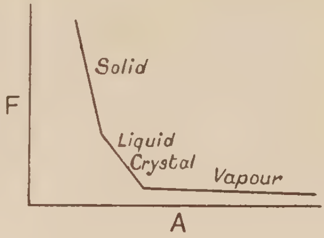
The transition of films from one state to another can as we have noted be effected by alteration in both temperature and pressure. We have already commented on the ready conversion of palmitic acid from the solid into the smectic state by decrease of pressure alone on feebly acid solutions, and on the transformations noted by Labrouste and studied by Adam of myristic acid into the expanded state by elevation of the temperature.

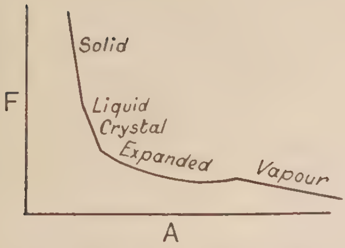
There is an almost exact parallelism between these two-dimensional changes of state for fatty acid films and those observed in the corresponding solid, liquid-crystal, liquid and vaporous states of bulk matter. We may note from the figure, a typical triple-point diagram, that the effect of change in pressure at a temperature T_1 causes sublimation and solidification; at T_2 the change proceeds through the phases solid, liquid-crystal, vapour; at T_3 solid, liquid-crystal, liquid, vapour; and at

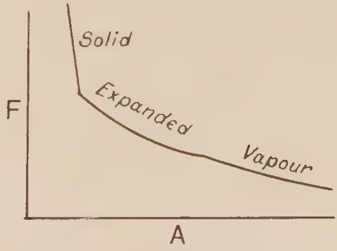
T_4 merely the liquid vapour transition. The force/area curves obtained directly by experiment are in exact accord with these changes; we can observe clearly the following succession of curves on raising the temperature, the type of phase being inserted in the diagrams.


P
Solid
Liquid Crystal
Liquid
Vapour
T_1
T_2
T
T_3
T_4


F
Solid
Vapour
A

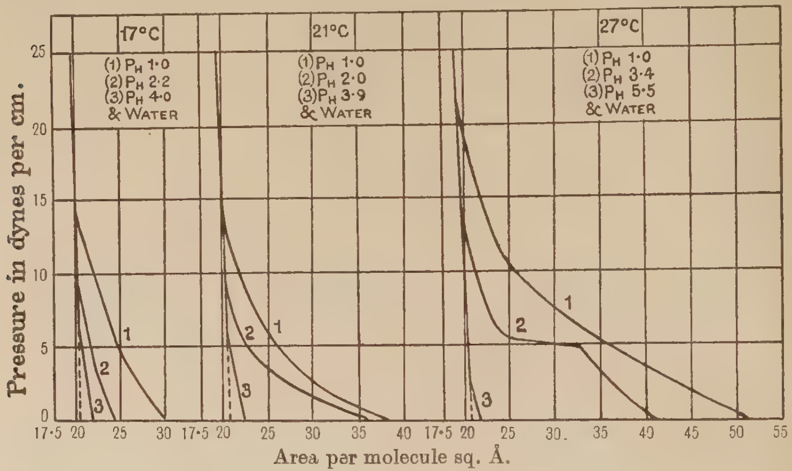

F
Solid
Liquid Crystal
Vapour
A


F
Solid
Liquid Crystal
Expanded
Vapour
A


F
Solid
Expanded
Vapour
A

The form of the triple-point diagram for these two-dimensional equilibria is likewise similar to the P, T diagram given above for a three-dimensional system, since the film area successively diminishes as we pass through the sequence of phases, vapour, liquid, liquid-crystal, solid, whilst the exact slopes of the lines bounding the phases are readily calculated with the aid of the modified Clapeyron-Clausius equation.

That an alteration in the acidity of the substrate can effect the conversion of a film of a fatty acid from one state to another can be observed from the following data for pentadecylic acid.



The Force/Area Curves for Pentadecylic Acid.

Temperature ° C.	P_H	Area/molecule sq. Å.	Nature of film
17	1·0	30·2	Partially expanded
	2·2	24·3	Low pressure form condensed
	4·0	21·8	Condensed
	Water	21·8	,,
21	1·0	39·5	Nearly completely expanded
	2·0	37·5	,, ,, ,,
	3·9	22·0	Condensed
	Water	22·0	,,
27	1·0	51·5	Completely expanded
	3·4	41·6	Nearly completely expanded
	5·5	21·6	Condensed
	Water	21·6	,,

It will be noted that as the solution is rendered more acid transition from the solid condensed through the liquid condensed to the expanded can be effected. A similar expansion can be obtained with a base such as heptadecylamine when placed upon strongly alkaline solution of P_H 13·2.

This increase in tendency to expand as the adhesion of the polar group to the substrate is weakened by ionic adsorption below the film (see Chs. II and VII) suggests that expansion is effected by a process of increasing the molecular tilt. A brief consideration of the structure of a terminal group such as —CH_2OH on a hydrocarbon chain indicates that the polar —C—OH group cannot lie along the axis of the chain and consequently, if the —C—OH be immersed vertically in the solution for any definite film area, the hydrocarbon chain must be tilted. If we make the assumption that this condition is fulfilled in the crystalline or solid condensed state at zero pressure, the angles which the long axis of the chain makes with the direction of the effective polar head can readily be calculated.

8. The rigidity of Films.

The force/area curves of the solid condensed state for the majority of film-forming materials are linear, an indication that the films obey Hooke's law and may therefore be considered as elastic sheets. The rigidity of such films can be measured by observation of the displacement effected on a portion of the film on application of a stress. Mouquin and Rideal (*Proc. Roy. Soc.* A, CXIV. 690, 1921) effected such measurements by rotation of a disc below such a film, thus exerting a drag on the film through the intermediary of the viscosity of the water. The displacements of portions of the film were measured by observing small dust particles on the surface of the film through a microscope, and proof that the elastic limits of the film were not exceeded was found in that when the rotation of the disc was stopped the particle under observation sprang back to its initial position.

If the displacement of the particle be δ at a distance r from the axis for an angular rotation velocity of Ω, when the disc of radius a is immersed to a depth h in water of viscosity η, then

$$\delta = -\frac{\Omega\eta}{8\bar{\mu}h}(r^3 - a^2 r),$$

where $\bar{\mu}$ is the coefficient of rigidity.

From 15° C. to approximately 30° C. the rigidity of the films of these two acids is almost independent of the temperature, that of palmitic acid falling uniformly from 30° C. to very low values (*ca.* 5 dynes per cm.) at 40° C.

The following values were obtained:

Palmitic acid $\eta = 0{\cdot}0101 \quad a = 5{\cdot}0$ cm.					Stearic acid $\eta = 0{\cdot}0101 \quad a = 5{\cdot}0$ cm.				
$\frac{2\pi}{\Omega}$ secs.	h cm.	r cm.	δ cm.	$\bar{\mu}$ dynes/cm.	$\frac{2\pi}{\Omega}$ secs.	h cm.	r cm.	δ cm.	$\bar{\mu}$ dynes/cm.
12	0·12	4	0·02	9·75	16	0·15	4	0·011	10·7
8	0·12	4	0·032	9·7	20	0·15	4	0·009	10·3
6	0·12	4	0·041	9·6	11	0·20	4	0·012	10·4
11	0·10	3·5	0·042	8·0	16	0·20	4	0·009	10·0
15	0·10	3·5	0·023	10·0					

Taking the thickness of the film in adhesion as 20 Å. for palmitic acid and 21 Å. for stearic acid, we obtain $4{\cdot}9 \,.\, 10^7$ dynes per cm.^{2} for the rigidity of the films comparable to the value of $1{\cdot}6 \,.\, 10^7$ dynes per cm.^{2} obtained for rubber.

The compressibility of films in the solid condensed state is very similar to that for the material in bulk; thus Adam obtained a one per cent. decrease in area for films of aromatic substances for a pressure increase of 5·8 dynes per cm. If the thickness of the film is 6 Å., the equivalent pressure is $97 \,.\, 10^6$ dynes per cm.^{2}, whilst for liquid benzene a volume decrease of one per cent. is found with a pressure increase of $113 \,.\, 10^6$ dynes per cm.^{2}.

9. The collapse of Films.

We shall have occasion to note that the conditions of equilibrium of a film with a lens are defined by the "equilibrium film pressure" which, whilst rising to quite large values of fatty acids on alkaline substrates, may be very small on acid solutions. Films artificially prepared by spreading with the aid of a volatile solvent will necessarily be unstable if the pressure applied in the troughs exceeds this equilibrium spreading pressure. Thus on weak acid solutions the films will be relatively unstable to compression as noted by Langmuir and Adam.

The effect of the collapse of a film by pressure is to make the surface visible by local thickening where the groups of the molecules have been ejected under the strain. The ejected molecules appear to behave as small nuclei for crystallisation. Since, in general, a clean film can be compressed to pressures exceeding the crystal equilibrium pressure, thus giving rise to conditions of metastability, it is a difficult matter to obtain the exact value of the film pressure when in equilibrium with the ejected nuclei of a collapsed film. Lyons (*loc. cit.*) has obtained the following values for palmitic acid at 21° C.

Solution	P_H	Collapsed film equilibrium pressure dynes per cm.	State of film at this pressure
Hydrochloric acid ...	1·4	11·0	Liquid
Citrate phosphate buffer	3·1	10·0	,,
	4·8	12·0	,,
	6·7	16·3	Solid

On the more acid solutions these equilibrium pressures are below the pressure at the intersection of the two force/area curves for the acid, and therefore the transition may be represented, following Langmuir, by the equilibrium

Liquid unimolecular film $\rightleftarrows$ solid multimolecular nuclei.

Owing to the effect of hysteresis the film pressure may rise above the solidification value before rupture occurs, but it always liquefies as the pressure falls to the equilibrium value.

On the more alkaline solutions the film when in equilibrium with the collapsed film is definitely solid.

These equilibrium pressures, probably owing to the distorted structure of the nuclei, are much larger than the equilibrium pressures between macrocrystals of palmitic acid and the unimolecular film under identical conditions (see p. 129).

10. The dissolution of Films.

It was noted by Adam (*Proc. Roy. Soc.* A, XCIX. 336, 1919) that condensed films of palmitic acid showed a small slow decrease in area on a solution at P_H 8·5, whilst on the more alkaline solution of P_H 10·0 this decrease in area took place so rapidly that he could obtain no force/area curves. The rate of solution of films of palmitic acid in buffer solutions of various alkalinities has been investigated by Lyons and Rideal (*Proc. Roy. Soc.* A, CXXIV. 344, 1929), who found that the rate of solution was appreciably enhanced by increasing alkalinity and the temperature and that it was slightly increased by increasing the pressure.

It was found that between P_H 8·5 and 13·0 complete solution of the film does not occur, but that a residual insoluble film of approximately half the original area is left. On fresh buffer solutions in the absence of any dissolved soap the solution process is autocatalytic.

A few of the values for the maxima of the rates of solution are given in the following table:

P_H	Pressure dynes per cm.	Temperature ° C.	Maximum rate of decrease in area (% of initial area per minute)
9·2	7·5	18	7·8
9·2	15·0	18	8·7
9·2	7·5	28	8·7
9·5	7·5	18	8·1
9·8	7·5	28	10·0
9·8	15·0	28	17·9
10·3	7·5	18	11·6

It is probable that solution of the film proceeds at various places in the film surface, and the molecules entering the underlying solution protect the residual film from solution. This residual film may therefore be regarded as a double film of orientated molecules of palmitic acid and sodium palmitate with their polar heads orientated together in such a way that inert hydrocarbon chains are exposed both to the air-surface and to the underlying solution, thus forming a half immersed elementary bimolecular leaflet which is the structural unit of soap films (*vide infra*).

The pressure of a unimolecular and a bimolecular film of palmitic acid formed in this manner in equilibrium with a crystal of the acid are widely different and a few values are given in the following table:

Temperature 21° C. P_H	Equilibrium pressure in dynes per cm.	
	Unimolecular film	Bimolecular film
8·2	11·6	4·8
8·8	13·1	3·6
9·4	14·5	3·6
9·5	14·7	3·6
11·4	18·3	3·0

The change in equilibrium pressure with the temperature over the range P_H 9·4 to P_H 11·4 was found to be almost constant and equal to 0·44 dyne per cm. per ° C. Inserting this value and placing $A_{\text{film}} = 10 \cdot 3$ Å. in the Clapeyron equation, we obtain 1,870 calories per grm. mol as the latent heat of spreading for such a film.

11. Complex and colloidal films.

The films to which we have devoted our attention in the previous sections are essentially unimolecular, and as we have noted may be regarded as the two-dimensional analogues of the solid, smectic, liquid and vaporous states of three-dimensional matter. On compression of such, fracture takes place and small nuclei are ejected from the film. Fatty acids spread by means of a solvent on an alkaline substrate we have noted undergo partial solution with the eventual formation of a bimolecular film. If the fatty acid be dissolved in caustic soda, i.e. in the form of a colloidal solution, and is then spread on acid solutions, Gorter and Grendel (*Proc. Kon. Akad. Amst.* XXIX. 9, 1926) have noted that the limiting areas are much smaller than correspond to a unimolecular film, and further observed that in some cases the films formed in such a manner were not always visibly homogeneous but appeared to possess colloidal aggregates on their surface. Whilst Gorter and Grendel's picture of these aggregates as containing polar groups orientated to their outer surfaces is not in agreement with the views we have previously expressed, yet we may certainly regard these films as composite, being in part at least multimolecular, and formed as a result of the unimolecular spreading incorporating portions of micelle in the resulting film. Such films are of course not necessarily stable (see p. 110). It is interesting to observe that the minimum area obtained by them was occasionally only one-third of the corresponding area for a unimolecular film. This value leads one to suspect that relatively thick films or at least layers of acid soap may be built up on aqueous surfaces in this manner. We shall have occasion to note in the case of soap bubbles that there is evidence for the existence of definite laminae.

The unimolecular character of these films is dependent on the adhesion of the polar group for the substrate, the magnitude of which can be measured by means of the spreading coefficient. If we examine the behaviour on compression of substances possessing small adhesions, i.e. materials with but feebly polar groups, we might anticipate that the films of these materials would be very fragile and that on compression very thick multimolecular aggregates in the film might be formed. This point has been examined by Harkins (cf. Harkins and Morgan, *Proc. Nat. Acad. Sci.* XI. 637, 1925), who states that a number of materials of small adhesions on compression are converted into thick multimolecular films before collapse occurs. A few of his values are incorporated in the following table.

Substance	At zero compression		At collapse	
	Area	Thickness	Area	Thickness
Hexachlor benzene ...	5·2	45·0	0·95	248·0
α-brom. naphthalene ...	1·5	187·0	0·6	405
Phenanthrene	5·6	47·0	2·0	120·0
Triphenyl methyl cyanide	5·2	70·0	5·0	120·0

According to Harkins such substances as phenanthrene exhibit but a small area when spread, the thickness being of the order of some five molecules which increases to more than ten on compression before collapse occurs.

No tests for uniformity of the film were made, and since films of dibromanthracene can be made visible by strong illumination almost parallel with the surface, these "multimolecular" films may actually possess a crystalline structure and consist in general of unimolecular films containing embedded crystals or micelles, as observed by Gorter and Grendel in the case of soap films.

We may conclude that apart from a bimolecular leaflet in certain soap solutions the evidence for the formation of uniform multimolecular films is not very conclusive.

In these films the molecular weight of the material forming the film is small and in consequence the disintegration of such films results in molecular dispersion. Substances as varied as isoprene, amino acids, cellulose acetate and nitrate can exist in highly polymerised states; thus simple rubbers may be regarded with Staudinger as consisting of chains or ribbons of isoprene molecules, cellulose nitrate or acetate of linked units of derivatives ($C_6H_{10}O_5$). Attempts have been made to spread such substances both on water and on the surface of liquid mercury with the aid of suitable solvents.

Relatively thin membranes of collodion can be obtained by spreading on mercury from ether-alcohol mixtures (Walcott, *Ann. de Phys.* LXVIII. 496, 1899; Dewhurst, *Proc. Phys. Soc.* XXXIX. 39, 1926) or on water from amyl acetate (Barton and Hunt, *Nature*, CXIV. 301, 1924). Taylor has obtained celluloid films from 30 to 700 Å. thick on mercury (*J. Sci. Inst.* III. 400, 1926), whilst Keenan (*J.P.C.* XXXIII. 371, 1929) has made a very complete investigation of the films of a number of these polymerised materials. The majority of them when spread from a suitable solvent in a dilution of *ca.* 1 in 1600 on mercury form a solid film of irregular outline, the area and consequently the thickness being readily determined. He found that the area was dependent on the viscosity of the solution; a few of the values obtained are given below.

Films of various types of cellulose nitrate in acetone.

Viscosity seconds	Area $Å.^2$	Thickness Å.
3025·0	296	2·80
0·2	168	5·00
775·0	202	3·97
13·5	186	4·55
2·1	170	4·88

The thickness of the elementary ribbon or band of the cellulose is thus from 2·8 to 4·5 Å. In a similar manner the thinnest band of rubber was found to be 1·5 Å. Of isoelectric gelatine at P_H 4·8 a thickness of 7·5 Å. was found in agreement with the data of Gorter and Grendel (see p. 118).

Devaux has likewise examined the spreading of sugars, starch and albumin on mercury.

Saponin films are also relatively thick and possess the characteristic of a skin rather than of a film.

Protein films.

Gorter and Grendel (*Proc. Kon. Akad. Amsterdam*, XXIX. 1, 1926; *Biochem. Zeit.* CCI. 391, 1928) have made a very extensive series of measurements on the spreading of fats and proteins on solutions of different alkalinities, and have measured the apparent limiting areas as well as the compressibilities for a number of such substances. The proteins were dissolved in caustic soda and spread on the water adjusted to a suitable P_H. As we noted in the case of the soaps, this method is liable to give somewhat unsatisfactory results owing to the fact that the liquid to be spread contains the solute in a colloidal state, and whilst unimolecular spreading always occurs small particles of colloidal micelle may be dragged out into the film by the spreading unimolecular layer. The final film is thus composite, consisting of unimolecular layer and micelle or nuclei, and it is certain that these two portions of the film cannot be in true equilibrium with one another over a range of pressures; inferences as to the thickness of the film from the spreading areas are clearly misleading. In spite of these objections however, Gorter and Grendel have obtained several interesting results. In the first place, over a considerable range of P_H the compressibilities are similar to those of the expanded films of fatty acids, and the protein films may thus be regarded as liquid in character.

Whilst the ratio of area to thickness may be obtained by direct measurement on assumption of uniformity of film, the actual molecular dimensions can only be obtained with the aid of a knowledge of the molecular weight and density of the protein. Three of their typical curves for the limiting areas on solutions of different P_H, together with the assumed molecular weights and densities, are given below.

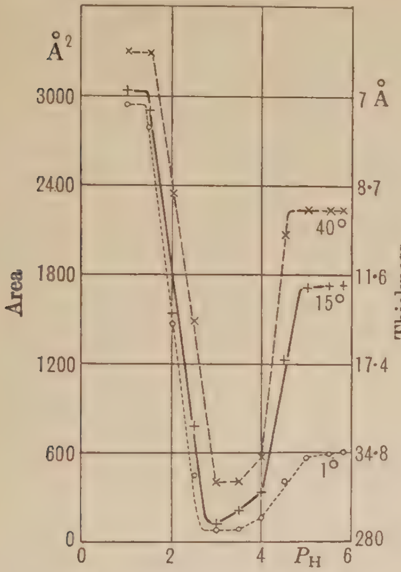


Fig. 1. Haemoglobin on HCl
Mol wt. = 16,000 Δ = 1·275

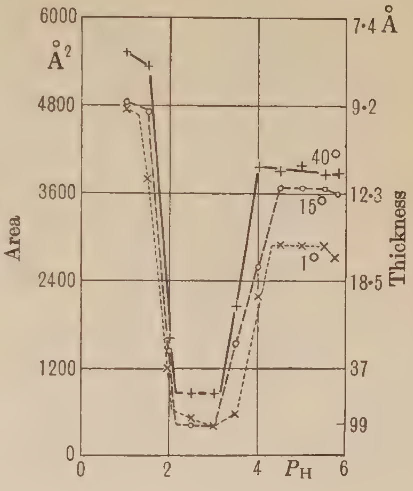


Fig. 2. Plasma albumin on HCl
Mol wt. = 34,000 Δ = 1·275

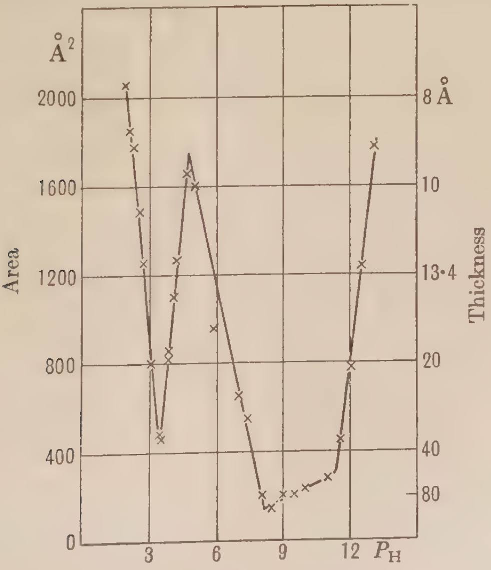


Fig. 3. Casein on P_H 2 to 13. Temperature 15°C.
Mol wt. = 34,000 Δ = 1·275

It will be noted that the proteins exhibit maximum areas of spread close to or coincident with their isoelectric points, whilst casein reveals two minima on each side of this point. As observed in the case of the simple fatty acids, the tendency to spread and to expand is increased as the adhesion of the polar groups for the underlying liquid is decreased; for such amphoteric substances this adhesion is a minimum at the isoelectric point, and the spreading tendency will thus be great. The minima in the spreading areas on each side of the isoelectric point are probably the points at which the maximum ionisation of the two salts $\mathrm{P}\overset{+}{\mathrm{H}}$ and $\mathrm{P}\overset{\prime}{\mathrm{O}}\mathrm{H}$ of the protein in the surface film occurs. As the ionisation is repressed, the surface adhesion is again lowered and the spreading tendency again increases.

The very large changes in areas observed with the proteins are remarkable; it appears possible that at the isoelectric point the protein molecules are spread in the form of flat plates in a uniform unimolecular layer of a thickness of only 7–8 Å. We cannot however assume with any degree of certainty that the films with smaller areas than those obtaining at the isoelectric points are homogeneous, and that the apparent contraction involves either a formation of multimolecular aggregates of the form observed in the soap films or alternatively a reorientation of the flat discs in an inclined or even vertical position, involving actual removal of some of the —CO—NH-groups from the water surface.

Soap films.

The analysis of soap foam by Miss Laing (*Proc. Roy. Soc.* A, cix. 28, 1925) shows that both acid and soap are present, the acid soap NaPHP possessing a greater stability than a soap of any other composition (cf. McBain and his co-workers, *J.C.S.* cxxxi. 2679, 1927; cxxxiii. 2166, 1928; Ekwall, *Acta Acad. Abo. Math. Phys.* vi. 3, 1927; Harkins, *J.A.C.S.* xlvii. 1854, 1925). The best methods of formation and many of the interesting properties of soap bubbles have been described by A. Lawrence (*Soap Films*, Bell and Co. 1928).

We have noted that the adhesion of the polar groups to water and to one another is much greater than the weak adhesion of hydrocarbon chains either to water or to one another. It is thus reasonable to assume, an anticipation verified by Perrin (*Ann. de Phys.* x. 160, 1918) and Wells (*ibid.* xvi. 69, 1921), that soap films may be made up of composite surfaces each of which consists of two layers of orientated molecules of soap, the outer surface of each side consisting of hydrocarbon chains and the polar groups held together with water as a sandwich between the orientated hydrocarbon chains. These elementary leaflets which will possess but little adhesion for one another may be built up to form thick films similar in structure to the crystalline fatty acids examined by Müller (see p. 96). The leaflets may slip over one another with great ease, thus providing the play of interference colours noticed in soap films. The elementary leaflet has in fact been shown by Perrin and others to be two molecules in thickness.

12. The permeability of bubbles and films.

The permeability of soap films has been examined in detail by Dewar, who showed (*P.R.I.* xxii. 193, 1917) that the rate of penetration varied with both the film thickness and the excess pressure in the bubble. A few of the values obtained for hydrogen are cited overleaf.

Bubbles which are made of glycerine and soap adsorb water when placed over a vessel containing water. The bubble thickens and eventually drops fall off. When the soap glycerine content of the bubble is reduced to 1 or 2 % by this process of drainage, drop formation ceases, the bubble becomes thin and black, and if maintained in a uniform temperature enclosure may be preserved for considerable periods. The rate of condensation of the water per sq. cm. of bubble surface is found to be inversely proportional to the age of the bubble and to obey the equation

$$\frac{dx}{dt} \cdot t = 0{\cdot}705,$$

where x = milligrammes condensed per sq. cm. and t is the time in days.

During this period the concentration of soap and glycerine in the bubble becomes progressively weaker, thus the rate of condensation is proportional to the concentration of the solutes in the soap film.

Black bubble.

Diameter cm.	4	6	8	10
Gas transfer in c.c. per sq. cm. per diem	·22	·14	·10	·053
Internal pressure mm.	·45	·30	·23	·18

Golden yellow bubble.

Diameter cm.	4	6	8
Gas transfer in c.c. per sq. cm. per diem	·285	·103	·050
Internal pressure mm.	·55	·103	·050

The rate of passage of substances or evaporation through films of different materials has not been subjected to any exhaustive investigation.

Rideal (*J.P.C.* xxix. 1585, 1925) studied the rate of distillation of water from one arm to another of a partially evacuated U-tube and determined the difference in rate on placing a film upon the surface of the water. The rate was found to be approximately inversely proportional to the surface film pressure. I and D. Langmuir (*J.P.C.* xxxi. 1719, 1927) determined from the rates of loss of weight of shallow troughs in air currents at different speeds the effects of films on the rate of evaporation of water and of ether.

If we define by R the resistance to evaporation as the difference between the reciprocals of the loss of weight per sq. cm. of film and water per second, we obtain from Rideal and Langmuir's data the following values.

Surface film	R evaporation in vacuo		Ratio of increase of resistance	
	25°	35°		
None ...	2·96	1·70	1	1
Stearic acid	303·0	165·0	102	97
Lauric acid	573·0	292·0	193	172
Oleic acid	853·0	617·0	288	362

Surface	Evaporation in air With no wind cm.^{2} sec. grm.$^{-1}$ R	With wind of 178 cm./sec. R
No film	430,000	68,000
Cetyl alcohol	520,000	128,000

It will be noted that cetyl alcohol, a particularly tenacious film, affects markedly the rate of evaporation of water, being in fact some seventy times as effective as oleic acid.

After insertion of ether into the water below the film, the rate of evaporation of ether from aqueous ether was determined by the rate of loss of weight of the troughs.

Langmuir's values are given in the following table:

Surface film	Temperature ° C.	$R \times 10^{-3}$ for ether		
		Wind velocity cms. per sec.		
		$v = 0$	$v = 61$	$v = 152$
No film ...	22·1	5·0	2·1	1·9
Oleic acid ...	27·5	36·0	32·0	32·0
Cetyl palmitate	22·5	32·0	33·0	30·0
Stearic acid ...	22·0	29·0	33·0	27·0
Cetyl alcohol ...	24·5	42·0	40·0	32·0

The effect of the film is to decrease the rate of evaporation of the ether in the ratio 7:1 without a wind and 17:1 with a wind of 152 cm. sec.$^{-1}$.

A few experiments with gaseous films such as caprylic and butyric acids gave somewhat inconclusive results by this method, but Bell (*J.P.C.* XXXIII. 99, 1929) has shown that the rate of evasion of chlorine from solutions in carbon tetrachloride is greatly affected by the presence of capillary active trichloracetic acid. The actual rate of evasion measured was only 1 % of the theoretical maximum rate, this being a limitation imposed by diffusion, but a reduction of 15 % in the observed rate was obtained in the presence of 1·4 % of trichloracetic acid (further additions causing no more diminution). Surface tension measurements by the drop-weight method revealed that $\Gamma_{\text{max.}}$ was attained between 1 and 1·6 % of the acid, in good agreement with the value of 1·4 % determined by the evasion method.

CHAPTER IV

LIQUID-LIQUID INTERFACES

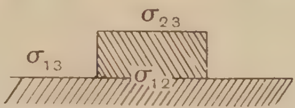
1. Introduction.

There exists as we have noted a separate phase at the interface between a liquid and a gas. The magnitude of the vapour-liquid interfacial energy is markedly dependent on the composition of the liquid, and although experimental data are somewhat scanty the surface energy is also affected by the nature of the gas in contact with it. It is to be anticipated that at the interface between two immiscible liquids a similar new interfacial phase will come into existence possessing a definite surface energy dependent on the composition of the two homogeneous liquid phases.

The study of the interfacial liquid-liquid phase however is complicated by several factors, of which the chief is the mutual solubility of the liquids. No two liquids are completely immiscible even in such extreme cases as water and mercury or water and petroleum; the interfacial energy between two pure liquids will thus be affected by such inter-solution of the two homogeneous phases. In cases of complete intersolubility there is evidently no boundary interface and consequently no interfacial energy. On addition of a solute to one of the liquids a partition of the solute between all three phases, the two liquids and the interfacial phase, takes place. Thus we obtain an apparent interfacial concentration of the added solute. The most varied possibilities, such as positive or negative adsorption from both liquids or positive adsorption from one and negative adsorption from the other, are evidently open to us. In spite of the complexity of such systems it is necessary that information on such points should be available, since one of the most important colloidal systems, the emulsions, consisting of liquids dispersed in liquids, owe their properties and peculiarities to an extended interfacial phase of this character.

2. On the conditions limiting spreading.

If a drop of oil be placed upon the surface of a liquid in which it is not soluble, there exists at the moment of contact an unstable system in which three surface forces are operative at three interfaces. We will define by σ_{13}, σ_{23} the two liquid vapour and by σ_{12} the liquid liquid interfacial tensions. If



$\sigma_{23} + \sigma_{12} = \sigma_{13}$, it is evident that the system will be in equilibrium as no decrease in free energy of the system can take place by spreading or contraction of the drop.

On the other hand if $\sigma_{23} + \sigma_{12} > \sigma_{13}$, a decrease in free energy of the drop can take place on contraction of the drop to expose a greater liquid vapour interface for the second liquid. The edges of the drop then contract and the flattened drop of liquid tends to become more spherical and assumes the shape of a lens forming a re-entrant angle with the liquid. If the lens be large, we note (see Bancroft and Tucker, *J.P.C.* XXXI. 1681, 1927) its shape will be determined by the relative magnitudes of σ_{12} and σ_{23}; thus if $\sigma_{23} > \sigma_{12}$ the drop will be pushed down into the substrate, and if $\sigma_{12} > \sigma_{23}$ the drop will tend to stand up. A lens must possess a definite thickness. Thus if a thick layer of benzene be placed upon a water surface and allowed to evaporate, when it gets below a critical thickness it will, if contained in a small beaker, be in a state of slight tension. On forming a small hole in the layer it will break up into a number of small and stable lenses which can be made to coalesce if evaporation be prevented. This phenomenon of the rupture of an insoluble thick layer with the formation of small drops or lenses in equilibrium with a unimolecular film can frequently be observed with liquids as varied as water and paraffin, especially on metals (see Blodgett, *P.R.S.* A, LXXXV. 30, 1911; Hardy, *ibid.* A, LXXXVI. 612, 1912; Rayleigh, *Scientific Papers*, III. 424, 1902).

On the other hand if $\sigma_{23} + \sigma_{12} < \sigma_{13}$, spreading of the lens will cause a diminution in the free surface energy of the system, and a number of interesting cases are presented which we shall have occasion to discuss.

3. The spreading coefficient.

The decrease in free energy taking place when the oil spreads over an area of 1 sq. cm. is evidently $\sigma_{13} - (\sigma_{23} + \sigma_{12})$ and may be taken as a measure of the tendency of the oil to spread, a point first noted by Sir W. B. Hardy, and to the value of which the name "spreading coefficient" has been applied by Harkins.

In the following table are given a few values for water as substrate, chiefly from the data of Harkins, of the spreading coefficient for a number of liquids which spread, and for liquids which do not spread but form lenses; in this latter case the value of $\sigma_{13} - (\sigma_{23} + \sigma_{12})$ is evidently negative.

Spreading liquids at 20° C.		Lens forming liquids at 20° C.	
Liquid	Spreading coefficient	Liquid	Spreading coefficient
Octane	0·22	Carbon tetrachloride	Very small
Nitrobenzene	3·76	*p*-bromtoluene	– 1·29 (30°)
Benzene	8·94	Ethylene dibromide	– 3·19
Chloroform	13·0	Carbon disulphide	– 6·94
Ethyl bromide	17·9	Bromoform	– 9·58
Oleic acid	24·62	Liquid petroleum	– 13·64
Undecylic acid	32·04	Acetylene tetrabromide	– 15·64
Dimethyl ketone	42·37	Methylene iodide	– 26·46
Acetic acid	45·20		
Ethyl alcohol	50·40		

If the liquid forming the drop be volatile, evaporation may take place followed by condensation of the vapour on the liquid supporting the drop; in this way non-spreading liquids, e.g. carbon disulphide, may spread through the vapour phase on water.

4. On the mechanism of spreading and conditions of equilibrium.

We have noted that the conditions for spreading are determined by the values of the respective surface tensions such that

$$\sigma_{23} + \sigma_{12} < \sigma_{13}.$$

If a lens of a pure liquid of low surface energy σ_{23} be placed upon the surface of another of high surface energy σ_{13}, the value of σ_{12} characteristic of the interface is attained with extreme rapidity and as a result the drop is flattened. If a continuous supply of liquid be provided to the lens with sufficient rapidity it will continue to spread as a thick layer, forming the composite film of Gibbs or the secondary layer of Hardy. The total surface energy of this system is evidently $\sigma_{23} + \sigma_{12}$. Occasionally, due to chemical action or to the diffusion of capillary active substances to the interface, the value of σ_{12} sinks but slowly and as a result the lens originally forming a re-entrant angle may change its shape with time and may eventually spread. If the quantity of liquid forming the lens be restricted, a unimolecular film is formed by surface solution from the edge of the lens. If the liquid forming the lens be composed of two liquids each possessing markedly different values for σ_{23} and σ_{12}, the surface solution of the most capillary active form is frequently accompanied by spreading of relatively thick portions of lens which spread out as sheets (cf. colloidal spreading, p. 114), and these eventually break up to form small lenses floating in equilibrium with a unimolecular layer, e.g. a mixture of a hydrocarbon oil and oleic acid on water.

The exact mechanism of unimolecular spreading from the edge of the lens is not clear, but in all cases where $\sigma_{23} + \sigma_{12} < \sigma_{13}$ it is probable that the lens is stretched and thus flattened; this flattening of the lens is but the forerunner to surface solution which occurs most rapidly at the air-liquid interface to form a unimolecular layer. The system attains equilibrium when the rate of surface solution is exactly balanced by the rate of recondensation from the surface film; the surface tension of the liquid covered with the unimolecular film thus attains a finite lens equilibrium pressure σ_ϵ characteristic of the lens and liquid at that temperature.

The conditions of equilibrium are given by (see p. 126)

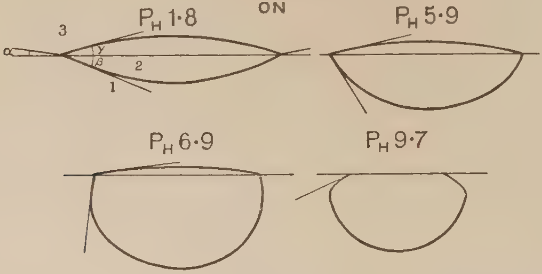
$$\sigma_\epsilon \cos \alpha = \sigma_{23} \cos \gamma + \sigma_{12} \cos \beta.$$

Since $\sigma_\epsilon < \sigma_{13}$, the lens must gradually contract as surface solution proceeds, until the conditions for equilibrium obtain.

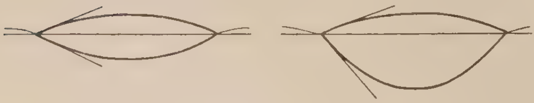
The angles of lenses of one liquid floating on another have been studied by Quincke (*Phil. Mag.* IV. 41, 454, 1871), by Hardy (*P.R.S.* A, LXXXVI. 610, 1912), and by Coghill and Anderson (*Bureau of Mines Tech. Paper*, 262, 1924), who calculated the angles from the thickness of the lenses and their depressions formed in the underlying liquid on the assumption that Neumann's condition of equilibrium, viz. equilibrium conditioned by the operation of surface forces, alone was valid.

The forms of various lenses examined by Lyons are depicted in the following diagrams. It will be observed that in the case of oleic acid the shape and submergence of the lens is very sensitive to changes in σ_{12} effected by changing the P_H of the solution. As the underlying solution becomes more alkaline the lens sinks deeper into it, the lower surface of the lens becomes more convex and the value of β rises steadily. This is in accordance with the simple theory of equilibrium based on the equations

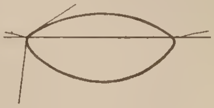
OLEIC ACID ON



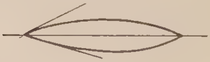
ETHYLENE DIBROMIDE ON WATER



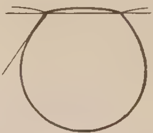
WATER ON ETHYLENE DIBROMIDE



PARAFFIN ON WATER



WATER ON PARAFFIN



$$\sigma_{13} \sin \alpha - \sigma_{12} \sin \beta + \sigma_{23} \sin \gamma = 0,$$
$$\sigma_{13} \cos \alpha - \sigma_{12} \cos \beta - \sigma_{23} \cos \gamma = 0,$$
$$\sigma_{12} + \sigma_{13} = \tfrac{1}{2} g\rho_1 (h_1 + h_2)^2 - \tfrac{1}{2} g\rho_2 h^2,$$

where σ_{13}, σ_{23} are the surface tensions of the liquids, ρ_1, ρ_2 their densities, and h_1, h_2 the heights of the upper and lower surfaces of the lens.

As σ_{12} diminishes the lens must gradually sink, the surface with the lowest surface tension being developed. Also β must increase so that $\sigma_{12} \sin \beta$ may still balance the vertical component of σ_{13}, and it must become re-entrant if the horizontal component of σ_{13} is less than that of σ_{23}.

The changes of shape observed are in agreement with these predictions. From the data given in the following table it will be seen that the conditions imposed by Neumann are by no means valid.

Liquid	Lens	$\sigma_{23} \sin \gamma$ dynes/cm.	$\sigma_{12} \sin \beta$ dynes/cm.	$\sigma_{13} \sin \alpha$ dynes/cm.	$\Sigma\sigma \sin \alpha$ dynes/cm.
HCl P_H 1·8	Oleic acid	7·4	− 7·5	1·5	1·4
Phosphate buffer 5·9	,,	7·3	− 9·8	0·0	− 2·5
6·9	,,	4·0	− 9·6	0·0	− 5·6
$C_2H_4Br_2$	Water	40·8	− 35·9	2·7	7·6
CCl_4	,,	34·3	− 44·4	− 5·0	− 15·1
Paraffin	,,	21·5	− 40·7	3·1	− 16·4
Water	Paraffin	9·3	− 12·3	1·5	− 0·5

The difference between the weight of the lens and the upward thrust of the displaced liquid is balanced by the surface tension of the supporting liquid acting around the edge. This factor determines the value of the angle α, and it is seen that this angle depends on the degree of submergence. The effect of these factors and of the internal pressure due to the curvature on the other angles presents a more complex problem. On the assumption that the lens surfaces are spherical segments the following equation may be deduced:

$$(\sigma_{23} \cos \gamma + \sigma_{12} \cos \beta - \sigma_{13} \cos \alpha)$$
$$- g \left[\frac{R}{2} \rho_2 - h_1 \rho_1 \left(r_1 - \frac{h_1}{3} \right) - h_2 (\rho_2 - \rho_1) \left(r_2 - \frac{h_2}{3} \right) \right] = 0,$$

where R is the radius of the lens, r_1, r_2 the radii of curvature.

In this equation the first set of terms represents the effect of the surface tension forces and the second that of the gravity and hydrostatic forces. The internal pressure forces are balanced for spherical segments.

A few of the data obtained by Lyons are tabulated below.

Liquid		Lens	R mm.	h_1 mm.	r_1 mm.	h_2 mm.	r_2 mm.	$\Sigma\sigma\cos\theta$	$\Sigma g\frac{R}{2}\rho_2$
HCl P_H	1·8	Oleic acid	2·30	0·32	8·1	0·60	5·36	1·4	0·8
Phosphate buffer	5·9	"	1·95	0·24	8·7	1·07	2·5	− 2·9	− 2·4
	6·9	"	1·11	0·10	14·1	1·37	1·5	− 3·8	− 3·9
	6·9	"	1·7	0·10	12·1	1·83	2·1	− 3·8	− 3·5
Water		Paraffin	1·75	0·40	4·75	0·28	8·3	− 3·5	− 3·7
"		$C_2H_4Br_2$	1·90	0·41	6·8	1·11	1·7	−11·6	− 8·0

A comparison between the values obtained in the final columns augment those noted in the previous table for $\Sigma\sigma\sin\alpha$, in confirming the view that the forces already discussed exert a marked effect on the angles of a lens in equilibrium.

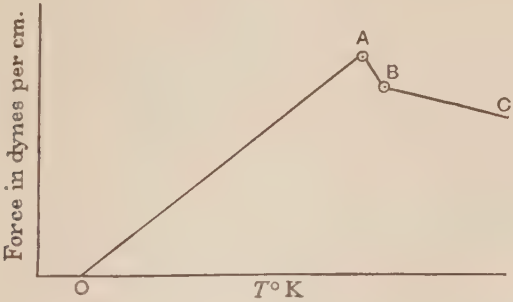
The lowering of the surface tension $\sigma_{13}-\sigma_\epsilon$ can be termed "the lens equilibrium film pressure" and a number of values have been determined not only for lenses of liquid oils but also for crystals of fatty acids by Cary and Rideal (*P.R.S.* A, CIX. 318, 1928). The wetting angles for solid crystals (Adam and Jessop, *J.C.S.* CXXVII. 1863, 1925) are not readily determined, since the adhesion of the water to the crystal surface varies with the nature of the surface, either a hydrocarbon or a polar head being presented as the planes are varied. The wetting angle for wax was found to be *ca.* 105° and for a plane with polar heads present from 20 to 50°.

In the table on p. 129 are given a few equilibrium pressures for solid materials on a water surface at the melting point determined by the ring method.

5. The heats of transformation of surface phases.

Either a liquid lens or a solid crystal of a spreading but insoluble and non-volatile substance when placed upon the surface of water will continue to spread, in the form of a unimolecular film, until at any definite temperature the surface tension of the water falls to a characteristic value for the substance; the lowering of the surface tension thus produced, $\sigma_{13}-\sigma_\epsilon=F$ may be regarded as a measure of the surface solubility of the solid or liquid under investigation (similar to the osmotic pressure in the case of bulk solution). The surface phase may however be either gaseous, solid, liquid or expanded, and the equilibrium pressure will likewise vary if the bulk phase be solid or liquid. The variation in the equilibrium pressure with the temperature for a number of solid and liquid organic insoluble substances have been determined by the ring method. As typical may be given the following curve for stearic acid.

Substance	Melting point ° K.	Equilibrium film pressure in dynes per cm. $F = \sigma_{13} - \sigma_\epsilon$	$\frac{dF}{dT}$ for solid crystal in dynes per cm. per ° C.
Undecylic acid	298	38·2	0·588
Lauric acid	318	35·1	0·548
Myristic acid	327	30·7	0·568
Pentadecylic acid	325	32·6	0·552
Palmitic acid	336	32·1	0·554
Stearic acid	344	29·9	0·553
Oleic acid	280	30·5	0·517
Hexadecyl acetate	294	34·4	0·637
Octadecyl acetate	305	30·7	0·667
Ethyl palmitate	300	19·4	0·669



It is found that no perceptible (to 0·5 dyne per cm.) lowering of the surface tension of the water occurs until the temperature reaches a well-defined value *O*. A few of these limiting temperatures are given in the following table:

Compound	Temperature of commencement of surface solution ° K.
C_{11} chain acid	233
C_{12} ”	254
C_{14} ”	273
C_{15} ”	266
C_{16} ”	278
C_{18} ”	290
Oleic acid	221
Hexadecyl acetate	240
Octadecyl acetate	259
Ethyl palmitate	271

We must imagine that some of the molecules in the crystalline solid have carboxyl groups wetted by the water on the line of contact; these groups although attached to the water cannot pull off the hydrocarbon chain at low temperatures. At 17° C., however, in the case of stearic acid the force of dissolution and the kinetic energy of the molecule are sufficient to permit of rupture. The molecule now floats freely on the surface of the water. During the course of time a number of molecules are so detached; they do not however exert any appreciable action on the tension of the water since every collision between free molecules is inelastic. In this manner a film of molecules upon the surface of the water then commences to pack and lower the surface tension. The point O (Fig. p. 129) may be considered as the equilibrium point of the system solid crystal, film and water.

From the point of view of the phase rule

$$P + f = C + 2,$$

we may regard the system as one component consisting of fatty acid, or as a two-component system fatty acid and water. In the latter case there is an additional restraint on the system in accordance with the expression

$$\Gamma_1 d\mu_2 = - \Gamma_2 d\mu_1 .$$

At O three phases exist in equilibrium, hence $f = 0$ or O is an invariant point. On elevation of the temperature the water phase disappears and the system becomes divariant. Along the line OA the surface film at first solid is observed to melt. No abrupt melting point can however be noted and no break is observed in the line OA.

At A the crystal melts and there are present three phases: solid crystal, liquid lens and film. The system is accordingly nonvariant.

The F, T curve beyond this point is again linear, but the surface pressure decreases rapidly with elevation of the temperature until the point B is reached where an abrupt change in the slope of the curve is noted. In many cases such as in the long chain esters the film is found to be condensed at A and expanded at B, thus AB is the expansion interval of Labrouste and Adam. For acids on the other hand, with the exception of stearic, the film is already expanded at the melting point and the portion of the curve AB is missing.

Since the equilibrium pressure F is a measure of two surface tensions

$$\sigma_{\text{oil}} + \sigma_{\text{interface}},$$

it is clear that in those cases where the portion of the curve AB exists, the interfacial surface tension must change rapidly with the temperature over the portion AB and move slowly over the region BC. In the film these two portions of the curve are associated with a transition from a condensed to an expanded film and with this analogy we may regard the oil-water interface as being capable of existing in two states, condensed and expanded. At B the oil-water interface is expanded and has the usual small temperature coefficient, at A the interface is condensed or partly expanded and possesses a high temperature coefficient although the interface may not necessarily expand at the same temperature as the film. Thus the interface may be condensed, partly expanded or completely expanded at the melting point, the actual state being determined by the length of the AB curve and the film area at the melting point.

A number of expansion temperatures, i.e. temperatures at B, together with the equilibrium pressures are given in the table on p. 132, which can be compared with the data presented on p. 102.

From the slopes of the various segments of the curves together with a knowledge of the areas of the molecules at the invariant points it is possible to calculate the latent heat of change from the bulk phase to the surface.

Compound	Temperature of expansion in ° K.	F equilibrium pressure in dynes per cm.
Stearic acid	350	26·3
Hexadecyl acetate	310	19·6
Octadecyl acetate	321	16·0
Ethyl palmitate	306	14·3

Thus in the case of stearic acid the slopes of the curves are

$$OA \qquad \frac{dF}{dT} = +\,0{\cdot}553 \text{ dyne per cm. per } ^\circ \text{ C.}$$

$$AB \qquad \frac{dF}{dT} = -\,0{\cdot}67 \qquad \text{,,} \qquad \text{,,}$$

$$BC \qquad \frac{dF}{dT} = -\,0{\cdot}153 \qquad \text{,,} \qquad \text{,,}$$

Writing the equations for the conditions of equilibrium of the film with the crystal at B, we obtain

$$d\mu = -\,S_1 dT + A dF \text{ for the film,}$$

$$d\mu = -\,S_2 dT + v dP \text{ for the crystal.}$$

Since P is constant $v dP = 0$, and by eliminating $d\mu$ we obtain

$$\frac{dF}{dT} = \frac{S_1 - S_2}{A} = -\,\frac{\lambda}{TA};$$

inserting the value $A = 20{\cdot}6 \times 6{\cdot}06 \times 10^7$ sq. cm. per grm. mol we obtain $\lambda = 5{,}620$ calories as the superficial latent heat of spreading of the solid acid and $\lambda = -\,9{,}000$ as the superficial latent heat involved in the spreading of the film from the liquid lens and the expansion of the liquid interface. Together we obtain $\lambda_f = 15{,}000$ calories as the latent heat of fusion of stearic acid.

In previous sections we have noted for substances containing a polar group that the tendency to spread is determined by the adhesion of the polar group for the substrate and that for fatty acids the magnitude of this adhesion can be affected by alteration of the alkalinity of the solution; a few of these values determined by Lyons (*Proc. Roy. Soc.* A, CXXIV. 331, 1929) are given in the following table.

Temp. ° C.	Equilibrium pressure dyne	Area/molecule sq. Å.	λ crystal-film cals. per grm. molecule	State of film
		*Myristic Acid on Dilute Acid**		
1	0·6	26·3	5910	Slightly expanded from liquid condensed
5	2·84	26·5	6040	Ditto.
10	5·68	28	6490	Partially expanded
15	8·52	34	8040	Fully expanded
20	11·36	33	7930	Ditto.
25	14·2	32·5	7940	Ditto.
30	17·04	32·5	8070	Ditto.
		Pentadecylic Acid on Dilute Acid		
17	13·7	20·2	4660	Solid condensed
21	16·0	19·8	4610	Ditto.
28	19·0	19·5	4660	Ditto.
		Palmitic Acid on Dilute Acid		
18	0·6	24·2	5620	Liquid condensed
		Palmitic Acid on Alkaline Solutions		
18	7–18	19·5–20·0	9100	Solid condensed

* Area measurements given by Adam and Jessop, *Proc. Roy. Soc.* A, CXII. 362, 1926.

It will be seen that on acids the heat change on spreading to form an expanded film is 8,000 calories, for a liquid condensed film 5,620 calories and for a solid condensed film 4,640 calories. The latent heat of spreading on alkaline surfaces to form a solid condensed film is 9,100 calories, a value much larger than the corresponding value on acid solutions. The increased attraction of the molecule for an alkaline surface is therefore paralleled by an increase in the latent heat of spreading over that surface.

6. On the rate of spreading.

An examination of the mechanism of spreading of solids on water has indicated that the process takes place in somewhat the following manner. At a certain critical temperature the magnitudes of the spreading coefficient and of the kinetic energy of the molecule have risen (together) to such a value that a molecule can be torn off from the crystal surface* exposed to the water. The molecules thus detached exert a "vapour pressure" which gradually rises until it reaches the critical value for the formation of an expanded film. As a result of such surface solution an expanded film (see p. 101) grows around the crystal surface at a definite rate. The rate of solution at any temperature is constant for a definite area of interface of a given material and the expanded film is gradually compressed. For slow rates of solution the surface tension of the water is hardly affected at all until the whole area of the surface is covered with such an expanded film. Further, the rate of solution is slow enough to push out the film already formed without any sensible pressure gradient occurring in the film from crystal to edge. On a limited area of water the surface tension commences to be lowered when the further surface solution of the crystal commences to compress the expanded film. Compression by surface solution continues until the equilibrium value F is reached.

An examination of the rate of such compression for expanded films reveals the fact that they obey a law of the type

$$\frac{dF}{dt} = k\,(F_0 - F),$$

where F_0 is the saturation value.

It may readily be imagined that the equilibrium finally attained is a dynamic one in which the rate of solution

$$\frac{dn}{dt} = k'$$

is balanced by the rate of return of molecules to the surface, or

$$\frac{dn'}{dt} = kF_0 \quad \text{or} \quad \frac{k'}{k} = F_0,$$

at a rate proportional to the surface pressure.

---

* Surface solution only occurs at the edge of the crystal exposed to water-air interface, and solution does not occur or only very slowly from the parts of the crystal immersed in the water.

Hence the rate of compression will be defined by the equation

$$\frac{dn}{dt} - \frac{dn'}{dt} = k' - kF = \frac{dF}{dt},$$

whence
$$\frac{dF}{dt} = k\left\{\frac{k'}{k} - F\right\} = k\{F_0 - F\}$$

in agreement with the results obtained by Cary.

A few of the experimental data are given below.

Influence of temperature on time required to cover an area of 56·9 *sq. cm. of water with a unimolecular film under zero compression of myristic acid. Length of water acid interface* 0·251 *cm.*

Temperature ° K.	Time in minutes
288	> 12
293	6·8
298	2·2
303	0·7
308	0·3
313	0·2

Rate of saturation of a surface of $N/100$ HCl *by solid myristic acid. Area of surface* 56·9 *sq. cm. Length of crystal water interface* 0·251 *cm.* $T = 25°$ C.

F dynes per cm.	t calc.	t obs.
0	—	2·05
3·22	2·81	2·85
6·44	3·95	4·00
9·66	6·50	6·80
10·31	7·76	8·10

If the film formed by superficial solution is an expanded film at low pressures but condensed at high pressures, it is found that the unimolecular character of the compression time curve is obeyed until a critical value of F is reached at which the expanded film no longer undergoes gradual compression but is converted into a condensed film. The surface pressure accordingly increases much more slowly with the time than it would if such a transformation to a material of smaller molecular area were not occurring. This is well exemplified in the rate of compression of films of myristic acid at 25° C. and at 18° C. At the higher temperature the film is always expanded up to the equilibrium value of F. At 18° C. conversion from an expanded film to a condensed film occurs at a pressure of 5 dynes per cm. It is important to note that the film spreading from the crystal is not being pulled out by a differential tension between the edge of the film and the water, but is being pushed out by the solution of molecules at the crystal surface.

In the case of oils the expansion rate is very rapid, and frequently the layer spreads out from the drop in multimolecular thickness showing interference colours. After a few seconds however (usually from two to three) the excess oil above that necessary to form "unimolecular thickness" is pulled back into the lens or more generally into a number of minute lenses formed from nuclei resulting from dispersion of the crystal drop. This phenomenon noted by Devaux does not appear to occur when pure oils are employed but may readily be observed if a small quantity of benzene be added to the oil. Early investigations on the rate of spread of oils on a water surface were made by Woog (*C.R.* CLXXIV. 162, 1922), who showed that the rate was dependent on the "attraction" of the oil for the surface and considered that it was proportional to the sum total of all the polar groups in the molecule and inversely as the viscosity of the spreading oil. He obtained an expression for the rate of spread in the following form $t_n = nt_1 - k(n-1)$, where t_1, t_n are the times required to cover the first and nth metre respectively.

Land and Volmer (*Zeit. physikal. Chem.* CXXII. 399, 1926) have measured the rate of spreading of olive oil containing a small quantity of fatty acid on the surface of water.

The rate of expansion of the disc at any instant was found to be inversely proportional to the cube root of the diameter of the disc, thus indicating that the distribution of pressure on the disc is constant, a state of affairs very different to that obtaining in the surface solution of crystals.

The following derivation due to Blasius (*Zeit.-f. Math. u. Phys.*

LVI. 1, 1908) permits us to deduce the observed rate of expansion from this assumption.

If a plate of thickness b and area l^2 cm.^{2} moves with a velocity v in the plane of the larger diameter through a fluid of viscosity η and density ρ, the force on the plate F is given by the expression

$$F = 1{\cdot}327\, b \sqrt{\eta \rho l v^3}.$$

Since the plate has but one side in the water which has $\rho = 1$, $\eta = 0{\cdot}01$ C.G.S. units,

$$F = \frac{1{\cdot}327}{2}\, b \sqrt{0{\cdot}01 l v^3}.$$

Taking the surface tension difference between the oiled water and water as $\sigma - \sigma_0$ over the thickness of the plate, we obtain $F = b\,(\sigma - \sigma_0) = 18{\cdot}6$ dynes per cm.

Hence on eliminating b we obtain

$$v = \sqrt[3]{\frac{4\,(\sigma - \sigma_0)^2}{1{\cdot}327^2\, l \eta \rho}} = \frac{42{\cdot}8}{\sqrt[3]{l}} \text{ cm. per sec.}$$

A few of the experimental data are given below.

Radius of disc mm.	Velocity in cm. per sec.
0·17– 0·58	67
0·92– 1·20	48
1·70– 2·50	33
4·18– 5·01	24
6·68– 7·52	20
9·19–10·02	16
11·84–12·75	15

Since the rate of solution of the crystal is constant, the rate of increase of area of the expanded film varies inversely as the radius of the circular film. If the spreading be determined in a narrow trough where the expanding area touches the side of the trough, the film would, if rigid, undergo compression in this direction and continue to expand at the normal rate over the other portion of the full surface. Actually the film is not rigid and an augmentation in the velocity of spread in the "wave" front is noted. Thus, if a drop of oleic acid be placed on water in a circular trough in a position half-way along the radius from the centre, it will be observed that the "wave" front, at first circular, begins to move with increasing velocity at the point where it comes in contact with the trough rim, and the two horns travelling round each side of the trough edge will arrive at the point on the continuation of the radius at the far end of the trough in the same time as the direct portion moving there by expansion.

One or two observations of some interest may be made on the spreading of mixtures. If a small quantity of a slow spreading material be dissolved in one that spreads rapidly and the mixture be placed on a water surface, a unimolecular equilibrium layer of the second is rapidly formed. In the course of time the slow spreading material arrives at the oil-water interface and if the magnitude of σ_{AB} for the second oil be less than that of the first, the lens may actually spread out into a thin sheet. Again, if two crystals of fatty acids be placed upon a limited area of water, the equilibrium pressure will be found to be that of the fatty acid of higher surface pressure. In the case of two lenses of liquid fatty acid the equilibrium surface pressure may actually be higher than that of either acid in the pure state. It is possible that the formation of solid solutions as well as of liquids of higher surface solubility than the pure substances might be revealed by careful examination of such systems.

The spreading of water containing electrolytes on mercury has been examined by Burdon (*Proc. Phys. Soc.* XXXVIII. 80, 1926) and Burdon and Oliphant (*Trans. Farad. Soc.* XXIII. 207, 1927). For a metal liquid interface the value of σ_{23} is dependent on the interfacial potential (Ch. VII), thus the spreading coefficient will vary with the change in potential. The spreading of water containing oxygen takes place with extreme slowness, on the other hand drops of water containing dilute acids both mineral and organic spread rapidly to cover a definite area and then the motion almost ceases. The area covered during the period of rapid spreading is such that a definite number of molecules of mercury *ca.* 10 are covered by each hydrogen ion present in the acid. The following figures were obtained.

By passing a current of 16 microamperes for one second ($1{\cdot}0 \,.\, 10^{14}$ electrons) in a direction such that the mercury was positive and the water negative, perfectly pure water could be made to spread by the discharge of negative ions over an area of one square centimetre.

Acid	No. of molecules per sq. cm. covered × 10^{14}
HNO_3	0·90
HCO	1·0
HBr	1·2
HCOOH	0·96
CH_3COOH	1·02
$(CH_2)_2H.COOH$	0·98

We shall have occasion to note in a subsequent section (Ch. VII) that there exists in general a potential difference between a metal and an electrolyte, and unless equilibrium conditions are already established ions will pass across the boundary to establish equilibrium and at the same time the ionic arrangement of the boundary layer must adjust itself so that the conditions both of chemical and electrical equilibrium is obeyed. This necessary electrical condition has to be fulfilled also in the case of mercury in contact with water by the adsorption of positive ions from the solution; these may be mercury ions formed by a surface chemical reaction which may be written in the form

$$\mathrm{Hg} + \mathrm{HOH} \rightleftarrows \overset{+}{\mathrm{Hg}}\,\overset{\prime}{\mathrm{OH}} + |\ \mathrm{H}_2 \text{ adsorbed } \mathrm{O}_2\ |$$

the liberated hydrogen being consumed except on a rapidly expanding mercury surface by oxygen dissolved in the water, the mercurous hydroxide supplying the necessary ions, a reaction which proceeds very much more slowly than adsorption of hydrogen ions which are present with the acid in solution.

7. Antonow's Rule.

A very significant observation connecting the interfacial tension between two liquid phases *in equilibrium* with the surface tension of each separately against the vapour phase was discovered by Antonow. The interfacial tension is equal to the difference between the two surface tensions. It is important to notice that we must deal with phases in equilibrium, since it often happens that the tension of the one pure liquid is greatly reduced by the addition of the second even though the solubility may be exceedingly small. In the extreme case, the solubility of one phase in the other is too small to be measured, as in the case of palmitic acid in water, but the surface tension of the solvent may, as we have already seen, nevertheless be reduced very much. The following examples* may be quoted in support of Antonow's rule.

Liquid	Surface tension			Interfacial tension		Temp. ° C.
	Aqueous layer	Oil layer	Pure oil	Calculated	Observed	
Benzene	63·2	28·8	28·4	34·4	34·4	19
Ether	28·1	17·5	17·7	10·6	10·6	18
Aniline	46·4	42·2	41·9	4·2	4·8	26
Chloroform ...	59·8	26·4	27·2	33·4	33·3	18
Carbon tetrachloride	70·2	26·7	26·7	43·5	43·8	17
Nitrobenzene ...	67·9	43·2	43·4	24·7	24·7	18
Amyl alcohol ...	26·3	21·5	24·4	4·8	4·8	18
Cresol	37·8	34·3	37·1	3·5	3·9	18
Amyl alcohol 5 % + Benzene 95 % ...	41·4	28·0	26·0	15·4	16·1	17
Cresol 5 % + Benzene 95 % ...	56·5	28·7	29·1	27·8	27·5	17

The agreement in the above table is very good. Equally good are the results found by Reynolds in the case of benzene and aqueous solutions of various substances which raise the surface tension of water.

In certain cases the interfacial tension observed initially was close to the calculated value, but fell lower with lapse of time, sometimes considerably: thus with water and a liquid paraffin mixture the surface tensions of the two phases were respectively 73·0 and 31·5, and the interfacial tension fell from 41·0 after five minutes contact to 15·1 after standing together for a day. In such cases a chemical change may be assumed, although it is not always easy to find a probable one.

Reynolds excepts from the general validity of Antonow's rule the tension of mercury and amalgams against certain electrolytes and immiscible liquids which react chemically. It is clear that the rule would be difficult to verify satisfactorily in the latter case; with mercury in contact with aqueous solutions (or with water) the apparent deviation from the rule is probably to be accounted for by consideration of the electro-capillary effects (Ch. VII).

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* Reynolds, *J.C.S.* cxix. 460, 1921.

Solute	Concentration	Surface tension			Interfacial tension		Temp. °C.
		Solution	Aqueous layer	Benzene layer	Calculated	Observed	
NaCl	0·1	72·2	64·0	28·9	35·1	34·9	18
,,	1·0	74·4	65·5	28·7	36·8	37·3	19·5
,,	5·0	83·5	72·0	29·1	42·9	42·5	17
NaOH	1·0	74·8	65·3	28·9	36·4	37·7	18
,,	5·0	84·5	72·7	29·0	43·7	44·7	17
H_2SO_4	0·5	73·0	62·5	28·0	34·5	35·0	25
,,	2·5	75·6	65·7	28·9	36·8	36·6	18
,,	5·0	77·4	66·2	28·9	37·3	37·1	18
$Na_2S_2O_3$	0·1	73·5	63·4	28·7	34·7	34·6	20
Glycerol	5·0	70·9	57·7	28·7	29·0	28·6	20
Sucrose	0·1	73·7	62·7	28·7	34·0	34·4	20
,,	1·0	75·3	63·0	28·9	34·1	34·1	18

(Concentrations measured in grm.-mols per litre.)

We may note that if we have the two liquids in separate vessels enclosed under one bell-jar so as to allow of free evaporation and condensation from one vessel to the other, the total surface tension in the vessel containing the liquid of higher tension will be unaltered if the other liquid distils over so as to cover the first with a thick film, for then we shall have two surfaces whose combined free energy equals that of the original surface. If on the other hand the liquid of higher tension were to distil over and form a thick film on the other liquid, the sum of the surface energies would have increased by $\sigma_A + \sigma_{AB} - \sigma_B = 2\sigma_{AB}$ for each unit of surface; the phase of lower surface tension must therefore remain uncontaminated by the other.

8. Interfacial surface tension and solubility.

Since the interfacial tension between two liquids can always be expressed as the difference between two surface tensions, interfacial tensions in general must necessarily be smaller than surface tensions, and may be very small indeed. As a rule, especially with a closely related series of compounds, the interfacial tension increases as the solubility in the second liquid diminishes. Thus at 20° C. the interfacial solution of alcohols against water are

Propyl	alcohol	0 (miscible in all proportions)
Isobutyl	,,	1·8
Isoamyl	,,	4·4
Octyl	,,	8·5

and the solubility diminishes in the same order.

Against mercury we have

Isobutyl alcohol	342·7
Secondary octyl alcohol	359·0

The order is the same, although the solubility of the liquids is so small as to be practically meaningless, so that solubility is not a helpful criterion in this case.

Let us denote by $\begin{cases} \sigma_A, \sigma_B \text{ the surface tensions of the pure liquids,} \\ \sigma_{A'}, \sigma_{B'} \text{ those of the mutually saturated phases,} \\ \sigma_{AB} \text{ the interfacial tension.} \end{cases}$

Then by Antonow's rule, $\sigma_{AB} = \sigma_{A'} - \sigma_{B'}$.

Now if the mutual solubility be not great, $\sigma_{B'}$ will not differ much from σ_B: but $\sigma_{A'}$ may however be very much less than σ_A, and the difference will as we have seen be greater the larger the surface concentration of B when dissolved in A. Thus the effect of B in lowering the surface tension of A against air is reflected again in the interfacial tension between the two liquids.

9. Influence of temperature.

The variation of interfacial tensions with temperature has been measured by Harkins in the case of a few organic liquids against mercury, and like surface tensions they diminish with rise of temperature.

The decrease of interfacial tension with rising temperature might normally be ascribed to increase in solubility. We have unfortunately no data with which to compare the interfacial tensions directly with solubility of a pair of partially soluble

Liquid	0°	10°	20°	30°	40°	50° C.	
Isobutyl alcohol	349·1	345·6	342·7	341·0	340·2	339·3	Interfacial tension against mercury
Secondary octyl alcohol ...	365·4	361·7	359·0	357·3	355·0	353·6	
Octane	377·2	375·8	374·7	373·4	372·6	371·3	
Benzene	—	361·3	357·2	353·7	351·4	349·8	
Surface tension of mercury	480	478	476	474	471	469	

liquids at different temperatures, but from the results of Whatmough* on the surface tensions of such phase pairs we can calculate the interfacial tensions from Antonow's rule. The following values are interpolated from his results.

ANILINE AND WATER.

(Critical solution temperature = 168° C.)

Temp. ° C. ...	15	25	35	45	55	65	75
Tension of aqueous phase	59·92	59·000	58·155	56·965	55·485	54·64	53·505
Tension of aniline phase	54·64	53·795	52·615	51·520	50·140	49·01	47·830
Interfacial tension calculated ...	5·28	5·205	5·540	5·445	5·345	5·63	5·675

METHYL ALCOHOL AND CARBON DISULPHIDE.

(Critical solution temperature = 40·5° C.)

Temp. ° C. ...	10	20	30	38·8
Tension of CH_3OH phase ...	27·49	26·51	25·44	24·66
Tension of CS_2 phase ...	27·75	26·67	25·49	24·66
Interfacial tension calculated	0·26	0·16	0·05	0·00

(Mean temperature coefficient of interfacial tension 0·0009.)

Goard and Rideal obtained the following values for the surface tensions of mutually saturated solutions of phenol and water.

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* *Zeit. phys. Chem.* XXXIX. 129, 1902.

PHENOL AND WATER.

(Critical solution temperature = 68·8° C.)

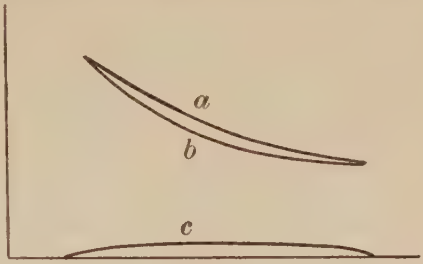
Temp. ° C.	0	10	20	30	40	50	60
Tension of aqueous phase	41·479	40·650	39·880	39·200	38·582	38·10	36·70
Tension of phenol phase	41·865	41·000	40·220	39·495	38·836	38·24	36·73
Interfacial tension calculated ...	0·386	0·350	0·340	0·295	0·254	0·14	0·03

It is a characteristic of two component systems forming one phase at a certain temperature that at this temperature the curve relating the partial molal free energy to the relative concentration of the components becomes horizontal. In other words, at the critical point

$$\frac{d\mu}{dN} = 0.$$

Since however $\Gamma = -\frac{d\sigma}{d\mu}$, or $-\left(\frac{d\sigma}{dN}\right)_A \left(\frac{dN}{d\mu}\right)_A$, it follows that for Γ to assume a finite value $\frac{d\sigma}{dN}$ must also be zero. Thus, as pointed out by G. N. Lewis (*Thermodynamics*, p. 253), at the critical point "a small change in composition will not change the surface tension between the liquid and air, regardless of the amount of surface adsorption of either constituent of the liquid." In addition, since for some distance on either side of the critical point the variation of the partial molal free energy with the composition is small unless the surface adsorption exhibits violent changes, the surface tension is largely independent of the composition.

In these examples, as one would expect, the interfacial tensions are small and diminish as the critical solution temperature is approached. The differences between the surface tensions of the two phases are generally too small to decide whether the interfacial tension approaches zero asymptotically in all cases, although such appears to be the case in the phenol water system: we notice however that the temperature coefficient is very small indeed, as is the case for surface tensions of liquids near their critical point, but to a still greater degree. It would be of considerable interest to have data for the surface and interfacial tensions of a pair of liquids such as nicotine and water which are miscible in all proportions except within a definite temperature range. Here we should expect to find curves of the type shown in the figure, where *a* and *b* represent the surface tensions of the two phases within the critical region and *c* their interfacial tension. The latter has no meaning either above or below the critical temperatures and must have a maximum at some intermediate point.



Lorenz and Liebmann* have measured the interfacial tension of molten lead against a mixture in molecular proportions of $PbCl_2$ and KCl between 450° and 600°. The results may be expressed approximately by the formula $\sigma = 211 + 0{\cdot}147\,(600 - t)$, though considerable experimental errors make the figures somewhat uncertain.

In bringing together the surfaces of two liquids to form a liquid-liquid interface heat is either evolved or absorbed during the process. This heat change may be termed with Harkins the heat of adhesion. The sum total of the surface energies of the two surfaces before contact less that of the interface after contact represents the total amount of energy given off or absorbed if the process be carried out isothermally, or

$$Q = \left\{\sigma_1 - T\frac{d\sigma_1}{dT} + \sigma_2 - T\frac{d\sigma_2}{dT}\right\} - \left\{\sigma_{12} - T\frac{d\sigma_{12}}{dT}\right\}.$$

Harkins gives the following values for the heats of adhesion of the following interfaces:

Interface	Heat evolved in calories per sq. cm.
Water-hexane	$2{\cdot}6 \times 10^{-6}$
Water-octyl alcohol ...	$4{\cdot}0 \times 10^{-6}$
Water-carbon tetrachloride	$2{\cdot}5 \times 10^{-6}$

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* *Zeit. phys. Chem.* LXXXIII. 459, 1913.

In the case of octyl alcohol the area of a molecule is *ca.* 25 Å.^{2} Thus a gm. molecule of octyl alcohol would occupy some $1{\cdot}51 \,.\, 10^9$ sq. cms. and the heat evolved would thus be of the order of 6000 calories per grm. molecule. If the liquid-liquid interface be formed by the condensation of a vapour on the clean surface of a liquid (σ_1) the heat of adsorption will be

$$Q = \left\{\sigma_1 - T\frac{d\sigma_1}{dT}\right\} + \lambda v - \left\{\sigma_{12} - T\frac{d\sigma_{12}}{dT}\right\},$$

where λ is the latent heat of vaporisation of the liquid which is condensed from the vapour phase. Harkins finds values of 3·25 and $3{\cdot}13 \,.\, 10^{-6}$ calories per sq. cm. for the heat of adsorption of isobutyl alcohol and octane respectively on a water surface.

Interfacial surface tension and chemical constitution.

Some interesting conclusions may be drawn from a consideration of the magnitude of the interfacial surface tensions of various liquids. The significance of these was first pointed out by Hardy (*Proc. Roy. Soc.* A, LXXXVIII. 303, 1913) and emphasised by Harkins (*J.A.C.S.* XXXVIII. 228, 1916; XLII. 700, 1920). We have noted that Antonow's rule only applies to mutually saturated solutions. If two pure liquids be brought in contact with one another in general

$$\sigma_A + \sigma_B > \sigma_{AB},$$

or during the process of mutual saturation as would be anticipated there will be a decrease in the free energy of the system. The magnitude of this decrease in the free energy is a measure of the chemical work performed and has an important bearing on the nature of the two liquids.

Harkins defines two terms, the work of cohesion or tensile free energy W_c which is the work done when a bar of liquid of unit cross-sectional area is pulled apart against the cohesive forces. It is thus numerically equal to twice the surface energy of the liquid. The work of adhesion W_a is similarly defined as the work required to pull apart a composite bar consisting of half of one liquid and half of the other, at the place of junction.

W_a is evidently defined by the decrease in free energy when the two liquids are brought into contact:

$$W_a = \sigma_A + \sigma_B - \sigma_{AB},$$

$W_c = 2\sigma_A$ for the first liquid and $2\sigma_B$ for the second.

Thus

for water $W_c = 145·8$ ergs per sq. cm.
for octane $W_c = 43·5$,, ,,
for octane-water $W_a = 43·8$,, ,,
for octyl alcohol $W_c = 55·1$,, ,,
for octyl alcohol-water $W_a = 91·8$,, ,,

According to Harkins' views, on breaking a bar of octyl alcohol the molecules of the alcohol on both sides of the plane of break should orientate themselves so that the break would occur with the least possible expenditure of work; in this case the molecules should orientate themselves so that the final break can occur between the ends of the hydrocarbon chains. This should lead to a value of W_c equal to that of octane. The higher figure actually observed Harkins attributes to imperfect orientation due to thermal agitation.

Liquid	$W_c = 2\sigma_C$ $\sigma_{H_2O} = 72·8$ ergs per cm.²	$W_a = \sigma_C + \sigma_{H_2O} - \sigma_{C.H_2O}$ ergs per cm.²	Spreading coefficient $W_a - W_c = \sigma_{H_2O} - (\sigma_{C.H_2O} + \sigma_C)$ for the water-liquid interface ergs per cm.² at 20° C.
N. hexane	36·8	40·1	3·3
N. heptane	40·2	41·9	1·7
N. octane	43·5	43·8	0·3
Ethyl bromide ...	48·3	66·2	17·9
Ethyl iodide ...	49·8	62·7	12·9
Octyl alcohol ...	55·1	91·8	36·7
Heptylic acid ...	56·6	94·8	38·2
Carbon tetrachloride	53·3	54·4	1·1
Chloroform ...	54·3	67·3	13·0
Dichlormethane ...	53·0	71·0	18·0
Benzene	57·72	66·63	8·91
Benzaldehyde ...	80·1	97·3	17·2
Benzyl alcohol ...	79·4	107·8	28·4
Aniline	83·2	109·6	26·4
Nitrobenzene ...	86·8	90·5	3·7
Carbon disulphide ...	62·8	55·8	− 7·0

In the case of the octyl alcohol-water interface the hydroxyl groups of the alcohol are immersed in the water, consequently when a bar of octyl alcohol is pulled away from the water, polar groups must be pulled from polar groups, so a high value of the work of adhesion should result from the orientation at such an interface. It thus follows that the difference between W_c for an organic liquid and W_a for that liquid and water should be a measure of the asymmetry of the molecules of the former, and as has already been observed, gives us a numerical value for the spreading coefficient (see p. 124). Compounds containing polar groups should give higher values for $W_a - W_c$ as is exemplified by the data given in the table on p. 147 for various liquids in contact with water at 20° C.

In a similar manner Harkins and his collaborators have determined the work of adhesion and hence the value of $W_a - W_c$ for a number of liquids in contact with mercury; some of the data are shown in the following table.

Liquid	$W_c = 2\sigma$ ergs per cm.^{2}	$W_a = \sigma_C + \sigma_{Hg} - \sigma_{C.Hg}$ ergs per cm.^{2}	Spreading coefficient $W_a - W_c$ for the mercury-liquid interface ergs per cm.^{2} at 20° C.
Water	145·6	173·8	28·2
Ethyl alcohol ...	44·8	134·4	89·6
Carbon disulphide	62·8	171·4	108·6
Methyl iodide ...	70·0	207·0	137·0
Benzene	57·8	147·7	89·9
N. hexane ...	36·8	116·4	79·6

Whilst the values for the work of adhesion and of cohesion fall with rising temperature, the difference $W_a - W_c$ is almost independent of the temperature as shown in the data presented on p. 149 given by Harkins (*loc. cit.*).

We note that the value of $W_a - W_c$ for aliphatic derivatives on water decreases with replacement of what are generally termed the polar groups by less polar ones in the following order —COOH, —OH, —Br, —I, —CH_3.

The interfacial surface tension may be markedly affected by a surface reaction occurring in the presence of traces of impurities.

A good example of such an effect has already been noted in the alteration of the spreading pressure for an oil containing a fatty acid and water containing acid or alkali.

System $C_6H_6.Hg$				System $C_4H_9OH.Hg$			
Temp. ° C.	W_c ergs per sq. cm.	W_a ergs per sq. cm.	$W_a - W_c$ ergs per sq. cm.	Temp. ° C.	W_c ergs per sq. cm.	W_a ergs per sq. cm.	$W_a - W_c$ ergs per sq. cm.
10	60·8	150·1	89·3	20	45·4	156·0	110·6
20	57·8	147·7	89·9	30	44·0	155·0	111·0
30	54·2	147·9	93·7	40	42·6	152·1	109·5
60	46·2	141·8	95·6	50	41·0	150·2	109·2

10. Interfacial tension of solutions.

In the case of the interfacial tension of two pure liquids we have had to deal with the superficial system in equilibrium with a two-phase two-component system of three dimensions. If we add to this system a third component the problem becomes still more complicated. The simplest case is that in which the added substance is soluble in one phase and completely insoluble in the other, the original liquids being themselves mutually insoluble. The change of interfacial tension should then run parallel to the change of surface tension of the liquid in which the third component dissolves.

If the original liquids are mutually soluble and the third component is soluble in only one of them, the mutual solubility will be diminished by its addition—according to Nernst's law, at low concentrations. The rise or fall of interfacial tension will thus depend on two superimposed effects, the change of surface tension of the better solvent owing to addition of the solute, and that in each of the two liquids due to diminished concentration of the other. The latter effect tends to increase the tension, while the former may work in either direction.

If the original liquids are again partially miscible, and the added component soluble in either, the mutual solubility may be increased; if so the interfacial tension will probably diminish whatever may be the effect on the surface tensions of the two pure liquids. Clearly, if sufficient of the third component be added to make the two phases completely soluble the interfacial tension must disappear altogether.

It is logical to conclude with the case where the new component is not appreciably soluble in either phase. At first sight it would appear unlikely that the interfacial tension could then be affected in either direction, yet this is possible. If the interfacial tension is increased by its addition to the system this substance will be adsorbed at the interface; if decreased, the added body will be more sparsely distributed at the interface or not appear there at all. It is easy to observe, at any rate, the appearance of a film of non-transparent matter at the interface, and the experiment has been carried out for a number of liquid pairs and solids by Hofmann (*Zeit. phys. Chem.* LXXXIII. 385, 1913) and by Reinders (*Koll. Zeit.* XIII. 235, 1913). Powders of different kinds of insoluble inorganic compounds were shaken up with water and an organic liquid: in a few cases the powder went completely into the aqueous phase, in much fewer the organic liquid contained practically all the suspension, but in the great majority the solid went preferentially or completely to the interface. We should conclude then that the interfacial tensions involved are diminished by the addition of most inorganic solids. The argument is not perfectly complete since the particles are comparatively so large that we ought also to consider the tension at each of the solid-liquid surfaces. To begin from another side, the solid will go to the interface if each liquid is adsorbed at the surface between the solid and the other liquid, that is to say if the mutual solubility is increased at the surface of the solid. (The case is very similar to that of catalysis at a solid surface.) The positive adsorption of the first liquid A at the surface of the solid S and the second liquid B will occur if the tension S/A is diminished by B: similarly the tension S/B must be diminished by A. But $A/B = S/A \sim S/B$, hence if A be the liquid with the higher interfacial tension against S, S/A must be lowered by B to a greater extent than S/B by A. The necessity for considering the solid-liquid interfaces become less when the solid particles are of less than three-dimensional magnitude as in the case of suitable colloidal solutions. Reinders found that colloidal gold solutions went to the interface when shaken with CS_2, ether or isobutyl alcohol: here probably we may simply say that the effect is due to a lowering of the interfacial tension. A dilute solution of gelatine goes to the interface when shaken with benzene.

As examples of the first case we may consider McLewis' (*Phil. Mag.* (6), XVII. 466, 1909) results for the interfacial tension of petroleum against aqueous solutions of metallic salts (and of organic substances). He found that lowering of the interfacial tension occurred with addition of $CuCl_2$, $AgNO_3$ or KCl—an unexpected result, since each of these substances raises the surface tension of water against air, and presumably does not influence that of the organic liquid, so that the interfacial tension might be expected to be raised. This case deserves closer investigation. That aqueous sodium glycocholate should lower the interfacial tension of the same is to be expected, since this salt is adsorbed also at an air-water interface. Similarly Harkins found that butyric acid lowers the surface tension of water-benzene: the maximum quantity of solute adsorbed at the interface agreed with that at a water-air interface. Strictly, this example should come into the second class, since the solute is soluble in both solvents.

The interfacial tensions of a number of aqueous solutions against mercury have been measured by McLewis*, Patrick and others. The tension was lowered by addition of all the solutes examined, including mercurous sulphate, salicylic acid, picric acid, neofuchsin, morphine hydrochloride, caffeine, aniline, sodium glycocholate. All of these substances except mercurous sulphate lower the surface tension of water, yet diminish at the same time the interfacial tension against mercury. It would be interesting to examine the effect of traces of these bodies on the surface tension of mercury, for if Antonow's law holds good the surface tension of mercury should be lowered by them even more than that of water. We should, in fact, expect to find contamination of the mercury surface due to adsorption. In no case does the interfacial tension of mercury appear to be raised by the addition of a solute to water, and qualitatively this fact agrees well with the well-known ready contamination of mercury surfaces.

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* See p. 51.

The most accurately determined example of the third class has already been cited, namely the effect of butyric acid on the interfacial tension of benzene-water. Harkins has found the concentration of acid in both layers for each pair of phases in equilibrium, but did not measure that of the second solvent. The mutual solubility must however almost certainly increase with the addition of a body soluble in either, and the interfacial tension will be diminished, due to adsorption of the solute and the greater resemblance of the two phases. Bubanovic* has also determined the interfacial tensions of the same solutions against olive oil, obtaining very similar results. He has also examined solutions of chloral hydrate.

On the other hand the surface tension of water against olive oil is practically unaltered by the addition of ethyl alcohol, chloroform, benzene, or xylene, all of which lower to a greater or less degree the surface tension of water against air, and in these examples we may conclude that the greater mutual solubility has had at least as great an effect on the tension as the tendency to adsorption of the solute. An interesting experiment would be to start with two partially miscible liquids and add a third which would finally yield complete miscibility, following changes of composition and interfacial tension simultaneously. A similar result would be achieved by taking for example a concentrated aqueous solution of ammonia and adding potassium carbonate until two phases were reached, one rich and one poor in this salt.

Meyer† has measured the interfacial tension of amalgams of the alkali metals against aqueous solutions of their salts, obtaining results similar qualitatively to those of Schmidt‡ for the surface tensions against air. The interfacial tension of mercury-normal KOH is reduced to 33 % of its value by the addition of 0·0224 % of potassium to the metal, and when the concentration of potassium is only 0·0011 % by weight the tension has already fallen to 54 %. In the case of sodium amalgam-normal Na_2SO_4 the surface activity is still more striking: for lithium amalgam-normal LiCl it is not quite so great (although lithium does not appear to lower the surface tension of mercury against air).

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* *Meddel. fr. K. Vetensk. Nobelinstitut,* II. 17, 1911.

† *Zeit. phys. Chem.* LXX. 321, 1910.

‡ *Zeit. f. Phys.* XXXIX. 1108, 1912.

Meyer's results also resemble those of Schmidt in the peculiarity that the rapid fall in the value of the surface tension does not begin at the very lowest concentrations of solute. The first addition of alkali metal indeed produces little effect on the interfacial tension, and there is a point of inflexion on the concentration surface tension at its steepest part. This behaviour appears to be characteristic of amalgams: the explanation is not clear and the phenomenon deserves further investigation.

11. Emulsions.

The emulsions consist of two liquid phases, one, the disperse or discontinuous and the other the dispersion medium or continuous phase. It is evidently possible to obtain with one pair of immiscible liquids two emulsions, the one the invert of the other with respect to the continuous and discontinuous phases. We have noted that the interfacial energies of immiscible liquids such as water and aniline, although not so large as are the computed values for solid-liquid interfaces, are by no means inconsiderable and may be as high as 30–40 ergs per sq. cm., whilst even higher values are obtainable when one liquid is a metal such as mercury. Such liquids when dispersed in water form exceedingly unstable emulsions comparable to the suspensions (see Ch. VI). The volumnar ratio of the phases does not readily exceed 1 in 1000 and eventual coalescence on contact due to thermal agitation, i.e. the Brownian movement, usually occurs relatively rapidly. Dilute emulsions in water thus prepared are negatively charged, and exhibit the phenomenon of electric endosmose, whilst they are relatively easily precipitated by the addition of electrolytes in which the cations are the effective precipitating agents. The volumnar ratio of the disperse phase may however be increased, and the emulsions rendered more stable with the aid of addition or emulsifying agents. Such emulsifying agents can increase the stability of an emulsion in two ways: (1) by the formation of a film round the disperse phase which on account of its mechanical strength prevents coalescence on contact, and (2) by lowering the interfacial surface energy to small values, thus reducing the tendency to coalescence. The emulsifying agent must consequently be one that goes to the interface between the two liquids, imparts to the interface mechanical strength and effects a marked lowering of the interfacial surface tension.

12. Limits of emulsions.

The disperse phase consisting of relatively minute drops, if imagined to be perfectly spherical and undeformable would, when increased in number or size until point contact between neighbouring spheres was obtained, yield a volumnar ratio of disperse phase to dispersion medium of 74 : 26 which would fix automatically the upper limits possible in emulsification. The experiments of S. U. Pickering however (*J.C.S.* XCI. 2002, 1902) have indicated that much higher values for the volumnar ratio may be obtained: thus with suitable emulsifying agents such as soap, paraffin could be dispersed in water until a volumnar ratio of 99 : 1 was obtained. The logical interpretation of the experiments is to assume that the disperse oil drops are not undeformable but may be flattened at the points of contact as the spheres grow in number or in size, until ultimately the dispersion medium is reduced to a thin film enclosing a number of pentagonal dodecahedra. For such an intimate contact, where the surfaces of the polyhedra are formed by means of a film, to be stable it is evident that the emulsifying agent must possess great mechanical strength but must at the same time not be too brittle, otherwise fracture may result and the emulsion be broken.

We should thus expect that such emulsions would be rigid, and actually they set to a stiff jelly-like consistency. These emulsoid jellies or greases are polyhedral in structure and are to be distinguished from the true "gels" which consist of a solid disperse phase in a liquid dispersion medium (see Ch. IX).

13. The emulsifying agent.

It has already been indicated that two types of emulsions may be obtained between two immiscible liquids *A* and *B*, the one consisting of *A* dispersed in *B*, the other of *B* dispersed in *A*. In order to impart the requisite degree of stability to such systems an emulsifying agent must be added such that it will lower the surface tension of such liquid and thus in accordance with the Gibbs equation go to the interface and there produce a film which possesses a certain amount of mechanical rigidity. Substances which exist in colloidal solution and effect a marked lowering of the interfacial surface tension may actually undergo coagulation to form a solid membrane at the liquid interface. Such membrane formations have been noted both at liquid-air interfaces and also at liquid-liquid boundaries; thus saponin (Ramsden, *Proc. Roy. Soc.* A, LXXII. 156, 1903) separates out at a water-olive oil interface, cellulose nitrate at a benzene-water interface (Holmes and Cameron, *J.A.C.S.* XLIV. 66, 1922) and gelatine at an oil-water interface (Nugent, *Trans. Farad. Soc.* XVII. 703, 1922). The discrepancy between the actual amount of emulsifying agent adsorbed at the interface and that calculated with the aid of the Gibbs equation has been shown (*loc. cit.*) to be due partly to the non-ideal character of the emulsifying agent in solution, e.g. colloidal soaps and dyes, and partly to the high surface concentrations obtained which we have noted approximate to a limit of saturation above which precipitation and other irreversible changes frequently occur. The nature of the emulsion is found to depend on the emulsifying agent employed; thus soaps on addition to oil and water produce an oil in water emulsion, whilst the calcium salts of the fatty acids produce the invert emulsion of water in oil. In the same way the solid basic sulphates of iron, copper and metal are effective in producing oil in water emulsions but soot produces the invert water in oil emulsion.

The stability of an emulsion is dependent on the amount of the emulsifying agent at the interface. Briggs (*Journ. Phys. Chem.* XIX. 210, 1915) has examined the adsorption of sodium oleate at a benzene-water interface by determining the amount of soap extracted by emulsification of the benzene and thus increasing the liquid-liquid interface, when the figures given overleaf were obtained.

These figures are in approximate agreement with values calculated with the aid of the Freundlich adsorption isotherm (see p. 182) but no definite conclusions may be drawn from them since the actual area of liquid-liquid interface in all probability was variable, being dependent on the amount of emulsifying agent present. The quantity of various soaps required to form a stable emulsion of kerosene in water has been determined by Griffin (*J.A.C.S.* XLV. 1648, 1923) for sodium oleate, potassium stearate and potassium palmitate, and by der Meulen and Riemann (*ibid.* XLVI. 876, 1924) for sodium ricinoleate.

Conc. soap grm. per litre	Grm. sodium oleate adsorbed per litre of benzene
0·60	0·17
1·18	0·28
3·18	0·40
6·36	0·44
13·85	0·48
21·03	0·49
26·01	0·54

The general method of procedure was to disperse a known volume of paraffin in water with the aid of the soap. The average diameter of the kerosene emulsion droplets was determined by counting with the aid of a microscope and hemacytometer, from which the total interfacial area could be calculated.

The emulsion was then allowed to separate and it was found on analysis of the soap content of the aqueous lower layer and the concentrated emulsion in the upper layer that the emulsion had abstracted soap from the solution. Owing to the fact that the fatty acids are soluble in the oil the hydrolysis of the soaps and the subsequent removal of the fatty acid in the oil phase had to be eliminated by the addition of caustic soda. In this way the true quantity of soap at the oil-water interface could be determined. Some of the results obtained are tabulated below.

	Conc. of soap mols per litre	Conc. of base mols per litre	Acid at interface, mols per litre	Area of interface $\times 10^{-3}$ per c.c. of oil in sq. cm.	Area of interface occupied by 1 molecule of soap, Å^2
Potassium stearate	0·100	0·01	·0043	7·60	29
Potassium palmitate	0·010	0·01	·0040	7·60	31
Sodium oleate	0·100	0·01	·0028	7·45	44

As a result of a number of experiments the mean areas of paraffin-water interface occupied by a molecule of the emulsifying soaps were obtained as follows.

	Mean area in Å.
Sodium oleate	48
Potassium stearate	27
Potassium palmitate	30
Sodium ricinoleate	39·2–105·6

It was found that if less soap were employed the emulsions were unstable. The experimental results agree with the conclusion that the soaps exert their emulsifying powers on oil-water mixtures by going to the interface and coating the interface with a layer of soap approximately one molecule deep.

As has already been noted in the case of the air-water interface the fatty acids are orientated with their polar carboxyl groups in the water phase; we might consequently anticipate that in the oil-water interface the same orientation would occur, the hydrocarbon chain being immersed in the paraffin phase and the polar —COONa or —COOK group in the aqueous phase.

That inverted emulsions are formed with sodium and calcium soaps respectively indicates that such orientation *per se* is not the factor responsible for the type of emulsion.

The effect of the addition of different emulsifying agents on the size of the emulsified particle as well as on the form of the distribution curve for the variation in size has been subjected to some examination. Finkle, Draper and Hildebrand (*J.A.C.S.* XLV. 2780, 1923) (see also Harkins, *Science*, LIX. 463, 1924) have examined the emulsifying powers of the stearates and oleates of the metals, both with reference to the mean size of particle produced as determined by microscopic examination as well as the type of emulsion and its stability. A summary of their results for the system benzene-water emulsified with oleates is tabulated overleaf.

The determination of the size-number distribution curve of emulsions by the microscopic method is liable to give erroneous results owing to the difficulty in estimating both the number and size of the smallest of particles present. Kraemar and Stamm (*J.A.C.S.* XLVI. 2709, 1924) have shown that the size-number distribution curve for oil in water emulsions may be obtained by observation of the rate of rise of the disperse phase in a manner similar to that developed by Odén (*Bull. Geolog. Inst. Univ. Upsala*, 16, 1916) based upon Stokes' law, by observing the rate of sedimentation and the measurement of the time-accumulation curve of suspensions. The radius of a particle is readily obtained from the rate of rise on the assumption of the validity of Stokes' law from the equation

OIL IN WATER.

Soap	Cs	K	Na
Life of emulsion	8 weeks	8 weeks	6 weeks
Mean radius of emulsion particle	14·5 mμ.	19·5 mμ.	27·5 mμ.

WATER IN OIL.

Soap	Ca	Ag	Mg	Zn	Al	Fe
Life of emulsion	1 hour	1 day	2 days	2 days	7 days	10 days

$$2r^2 = \frac{9\eta\bar{x}}{\Delta\rho \, . \, gt},$$

where $\bar{x}$ is the vertical movement in time t, η the viscosity of the medium and $\Delta\rho$ the difference in density between the two liquid phases.

As the less dense disperse phase rises into some of the supernatant dispersion medium, the density decreases and its change with time can be measured. Ten per cent. benzene in water emulsified with 0·5 millinormal potassium palmitate and oleate was employed and from the accumulation curve the distribution curves were obtained. It was found that change in the phase ratio caused but little change in the size of the particle, the mass maximum forming an average radius of 8·8μ with the palmitate and 11·1μ with the oleate.

Stamm and Svedberg (*J.A.C.S.* XLVII. 1582, 1925) have likewise employed Svedberg's (*J.A.C.S.* XLV. 910–943, 1923; XLVI.

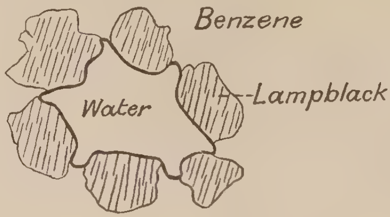
2177, 1924) method of observing the rate of movement of the disperse phase from observation of the change in intensity of light scattered by the particles when viewed at right angles to the source of illumination: the amount of scattered light is to a first approximation proportional to the number of particles present and to their mean area.

In this investigation the mass maxima for the radii of 1 % benzene emulsions emulsified with the palmitates of caesium, potassium and sodium (0·5 millinormal) were found to be identical, namely 4·4 μ, results not in agreement with the maxima based upon countings obtained by Finkle, Draper and Hildebrand. A shift in the mass maximum with 0·5 millinormal potassium palmitate was obtained as the disperse phase was decreased, the values of the diameters being

Vol. % benzene	15	10	5	2	1	0·5
Radius at mass maximum, in μ	10·2	8·8	8·8	6·4	4·5	1·7

The dispersity of an emulsion appears to depend as much on the mechanical method of preparation as on the nature of the emulsifying agent, although the relative size of the mass maximum according to Stamm (*loc. cit.*) appears to be somewhat influenced by the value of the spreading coefficient of the dispersed phase on water. The influence of the emulsifying agent both on the size of the mass maximum and on the type of emulsion formed has not yet been satisfactorily explained. Hildebrand (*loc. cit.*) suggested that both the size and in the limit the type of emulsion were determined by the relative cross-sectional areas of the hydrocarbon tails and of the polar heads, a large tail area and small head area as obtained in the trivalent salts permitting a curvature of the oil-water interface such that the oil became the external and thus the continuous phase; with monovalent soaps of the alkali metals the reverse was the case. This wedge theory of emulsions is, as we note, not supported by the work of Stamm. Numerous investigators have suggested that the type of emulsion found with various emulsifying agents is determined by the relative solubilities of the emulsifying agent in the two phases, that phase in which the emulsifier is more soluble being usually the external or continuous phase. We may note some exceptions: thus fatty acids form benzene in water emulsions although they are more soluble in the benzene phase. Soap is appreciably soluble both in amyl alcohol and water, yet amyl alcohol disperse phases always result irrespective of whether the soap is dissolved in water or the alcohol.

Emulsification produced by the addition of a dispersed solid to the two liquid phases must likewise be imagined to take place by reason of the solid going to the dineric surface (see p. 155) and being wetted but possessing a different angle of contact for each liquid. A microscopic examination of water emulsified in benzene stabilised with lamp-black indicated that this was actually the case.



Evidently the lamp-black is more soluble in the benzene than in the water phase. On increasing the concentration of lamp-black in the mixture the curvature of the particles increases and the mean diameter of the emulsion decreases as noted by Moore (*J.A.C.S.* XLI. 944, 1919) who obtained the following figures.

Weight of lamp-black per 10 c.c. kerosene in 30 c.c. N.NH_4Cl (grm.)	Mean diameter in mm.
0·4	·0551
0·6	·0452
0·8	·0367

The above arguments explain Bancroft's rule that a colloid emulsifier causes the phase in which it is soluble to be the external phase.

Donnan and Potts (*Zeit. Koll.* IV. 208, 1910) showed that the interfacial surface tension of a hydrocarbon water surface was lowered by the sodium soaps of the fatty acids and the lowering was dependent on the length of the chain as indicated by the following data.

Na salt of	Relative interfacial surface tension of oil-water interface referred to unity							
	$\frac{N}{400}$	$\frac{N}{200}$	$\frac{N}{100}$	$\frac{N}{80}$	$\frac{N}{40}$	$\frac{N}{25}$	$\frac{N}{20}$	$\frac{N}{10}$
Acetic	—	—	·995	—	·970	—	·937	·876
Propionic	—	—	—	—	·946	—	·901	·827
Butyric	—	—	—	—	·945	—	·909	·856
Valeric	—	—	—	—	—	·946	·908	·821
Heptylic	—	—	—	—	·939	—	—	·754
Caproic	—	—	—	·947	·921	—	·869	·780
Caprylic	·962	—	·895	—	·797	—	—	—
Capric	—	—	—	·835	·730	·630	—	—
Nonylic	·911	·856	·798	·753	·656	—	—	—
Lauric	—	·698	·532	·474	—	—	—	—
Myristic	·585	—	—	—	—	—	—	—

Although all the sodium salts are, as is indicated by the lowering of the surface tension, adsorbed at the interface the concentrations necessary to effect emulsification are so great for the salts of the short chain fatty acids that precipitation by the sodium ions results before the protective film can be built up. The first signs of emulsification are noted in the case of sodium caprate and sodium nonylate coinciding with the appearance of colloidal properties on solution.

The emulsifying agent need not possess colloidal properties in either phase, as is shown by the experiments of Holmes (*Colloid Symposium*, II. 135) who showed that methyl and ethyl alcohols would emulsify benzene in water, whilst propyl and butyl alcohols were inferior. Iodine will act as an emulsifying agent for ether and many esters in water. In this case also iodine is more soluble in the disperse phase than in the dispersion medium.

We may observe that it is not necessary to regard the process of emulsification as only dependent on the magnitude of the interfacial surface tension, but this necessarily decreases and the emulsification of two phases occurs more readily as the mutual miscibility of the phases increases: a substance soluble in both phases likewise increases the mutual miscibility.

If we regard the interphase between dispersion medium and disperse phase as composite, containing perhaps not only an orientated unimolecular layer of dispersing agent but also both phase materials in quantities sufficiently large that the interphase may be regarded as possessing different surface tensions on each side, i.e. as a composite layer, that side with the lower surface tension will naturally present a concave surface and will as a result form part of the continuous or external phase. This point of view has been emphasised by Bancroft (*J.P.C.* XVII. 515, 1914 and Tucker, *ibid.* XXXI. 1681, 1927) who points out that this suggestion is implicit in Gibbs' treatment of the possibilities of the formation of a separate phase at the surface where two different homogeneous phases meet (Gibbs, vol. I. p. 258). Lyons from an examination of the influence of the hydrogen ion concentration on the emulsifying powers of sodium palmitate on the system benzene-water finds that the stability of the water in oil phase is very low in solutions less alkaline than P_H 10, whilst the oil in water phase attains its maximum stability at that P_H. The stability of the former phase increases steadily to P_H 12, after which it falls due to salting out of the soap. Both types of emulsion were found to be unstable below P_H 8. These observations suggest that emulsification is dependent on the presence of an interfacial bimolecular leaflet (see p. 112, Ch. III), whilst a unimolecular film gives no tendency to emulsion formation.

A composite double film consisting of PNaHP and soap will be equally packed on either side. On solutions less alkaline than P_H 10 the lower or aqueous layer will be less densely packed than the upper layer at equilibrium, and the equilibrium state must be reached by one of two processes, a transference of molecules across the interface or the curvature of the boundary giving an oil in water emulsion. On very alkaline solutions water in oil emulsions are formed for similar reasons, whilst over the range where a symmetrical bimolecular layer is stable either form of emulsion is stable. On this view phase inversion by polyvalent ions is due to a relative increase in the concentration in the lower layer of the bimolecular leaflet.

14. The phase inversion.

We have noted that sodium salts of fatty acids will form an oil in water emulsion, whilst the addition of calcium salts yields a water in oil emulsion. On the addition of both sodium and calcium salts to the oil-water mixture it is evident that with suitable adjustment of the sodium soap to calcium soap ratio in the aqueous phase a condition of affairs may be reached such that the composition of adsorbed mixed soap at the dineric surface may be so adjusted as to give an equal curvature to each side of the interface. This state was first realised by Clowes (*Journ. Phys. Chem.* xxix. 407, 1916) who showed that with a sodium to calcium soap ratio equal to 4 : 1 (in molar ratio) the emulsion was unstable, a slight excess of sodium ions converting it into the oil in water type, a slight excess of calcium ions resulting in a water in oil emulsion. On the hypothesis of a unimolecular orientated soap film, indicated above, we must imagine that the interfacial film contains both adsorbed sodium and calcium soap. The inversion point is readily determined by the abrupt rise in electrolytic conductivity when the continuous oil phase is inverted to the continuous electrolyte containing water phase.

The inversion point of a number of salts for such emulsions has been investigated by Bhatnagar* (*J.C.S.* cxvii. 542, 1920), but unfortunately no data on the interfacial adsorption of the mixed salts are available as yet.

Some of Bhatnagar's data are tabulated below.

Emulsion: 10 c.c. water, 10 c.c. oil.
Emulsifying agent: potassium oleate.

Amount of soap in millimols	Millimols salt added to invert the emulsion				
	$Ba(NO_3)_2$	$Ca(NO_3)_2$	$Pb(NO_3)_2$	$Cr_2(SO_4)_3$	$Al_2(SO_4)_3$
0·080	2 × ·0199	2 × ·020	2 × ·0198	·017	·017
0·100	2 × ·0281	2 × ·027	2 × ·0252	·019	·017
0·151	2 × ·0410	2 × ·042	2 × ·0400	·028	·025
0·162	2 × ·0421	2 × ·044	2 × ·0440	·030	·027

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* *Trans. Farad. Soc.* xvi. 27, 1921.

According to his data the power of the various ions to reverse the phases followed this order:

$$Al^{\cdots} > Cr^{\cdots} > Ni^{\cdot\cdot} > Pb^{\cdot\cdot} > Ba^{\cdot\cdot} > Sn^{\cdot\cdot}, Ca^{\cdot\cdot}.$$

The explanation of stabilisation and phase inversion advanced above has, as already noted, received support from the experimental data on the effect of soaps and the salts of the fatty acids.

Emulsions can however be stabilised and inverted by the addition of salts of the inorganic and simpler organic acids. Thus with olive oil and water Clowes (*Koll. Zeit.* XV. 123, 1914) noted a phase inversion from oil in water to water in oil with the following salt pairs, the second salt producing the invert water in oil emulsion.

Salt pair		Mol ratio at inversion point
NaOH	$Ca(OH)_2$	2:1
Na citrate	$CaCl_2$	2:1
NaOH	$CaCl_2$	4:1
NaCl	$CaCl_2$	100:1

We have already referred to the experiments of Bhatnagar on the effect of inorganic salts on phase inversion of paraffin emulsions stabilised with soaps, and similar conclusions have been arrived at by Parsons and Wilson (*J. Ind. Eng. Chem.* XIII. 1119, 1921) utilising a purified mineral oil. They state however that no critical ratio of magnesium to sodium oleate could be obtained at which the emulsion was at the inversion point since two emulsions, the one the invert of the other, were always obtained. The work of Baur (see p. 364) has demonstrated quite clearly that the inorganic ions are oil soluble and that the difference between the partition ratios of cation and anion between oils and water may give rise to interfacial potential differences as well as interfacial concentration differences of cation and anion on each side of the interface. The difficulty of obtaining stable emulsions with a fat-free paraffin and inorganic soluble salts indicates however that these effects are relatively unimportant compared with those obtained with molecules which are definitely non-polar in character but containing a polar group. It is thus probable that the varying ratios of salts obtained for the inversion points with water-oil systems where the oil consists of a glyceride of a fatty acid are to be attributed to metathesis of the salt with traces of fatty acids present in the oil resulting in the production of soaps rather than the specific ionic adsorption. A careful examination of the emulsifying powers of inorganic salts on benzene or paraffin oil-water systems from which all traces of fatty acids or alcohols have been removed is evidently desirable in this connection. We find for example that neither Briggs (*J. Ind. Eng. Chem.* XIII. 1009, 1921) nor Harkins (*J.A.C.S.* XXXVIII. 242, 1916) could obtain any evidence for any stabilising action of sodium chloride in a water-benzene mixture. In commercial olive oil however a noticeable stabilisation is obtained but the aqueous solution becomes slightly acid, as would be anticipated if metathesis occurred with simultaneous adsorption of the liberated soap

$$NaCl + C_nH_{2n+1}COOH \rightarrow C_nH_{2n+1}COONa + HCl.$$

The soaps are in all probability not produced during emulsification by hydrolysis of the glycerides but from impurities present in the oils, since olive oil may be prepared in sufficient purity as not to be affected by the addition of caustic soda, the following figures being obtained by Donnan (*Zeit. phys. Chem.* XXXI. 42, 1899) for the drop numbers of purified and ordinary olive oil in water and caustic soda.

	Drop number in	
	H_2O	N/1000 NaOH
Ordinary	58	331
Purified	58	58

15. The ageing of emulsions.

By means of mechanical dispersion emulsions may readily be prepared; these however are unstable and on standing the emulsion may break and separate almost completely into the two phases. Instability of emulsions prepared with emulsifying agents such as saponin and protein matter may be ascribed to changes occurring in the protective film such as the irreversible coagulation noted by Ramsden (*loc. cit.*); the film thus becomes brittle and eventually cracks, leading to a separation of the emulsified phase. The cracking of emulsions stabilised with soaps on prolonged standing can be attributed to the gradual transformation of the dense soap film at the interface into curds as noted by McBain. In some cases however the protective film appears to become more resistant with age and the apparent stability of the emulsion increases instead of decreasing on standing. Such is the case with gelatine (Nugent, *Trans. Farad. Soc.* XVII. 703, 1922) where the gelatine film apparently gets thicker on standing.

Nugent noted that caustic soda broke a benzene-water emulsion stabilised with gelatine, and that the breaking was preceded by an inhibition period which increased with the age of the emulsion as instanced by the following figures.

Age of emulsion 0·4 % gelatine (hours)	Inhibition period on treatment with 0·5 N.NaOH (minutes)
0	0
2	35
6	45
12	55
24	60
48	70
72	75

Nugent assumes that the gelatine film increases in thickness with age and that the caustic soda strips the film layer by layer. The inhibition period is thus a measure of the thickness of the gelatine layer which evidently on this view increases with age. After 72 hours ageing the inhibition period was found to be constant at 75 minutes, the adsorbed gelatine film now being in true equilibrium with the gelatine in solution: this limiting inhibition period varies with the gelatine content of the emulsion as indicated in the following table.

Gelatine concentration %	Limiting inhibition period (minutes)
0·10	0
0·12	5
0·15	15
0·20	25
0·40	75

The mechanism of the breaking of the protected gelatine emulsion with soda is by no means clear. On the assumption that the gelatinate ion exerts but little stabilising action on the emulsion by reason both of its solubility and its negative charge we may regard the reaction as a simple diffusion reaction of hydroxyl ions with the gelatine surface,

$$\text{gelatine} + \text{NaOH} \rightleftarrows \text{Na gelatinate} + H_2O,$$

thus being a reaction of zero order, whence

$$\frac{dx}{dt} = k \quad \text{or} \quad x = kt.$$

The thickness of the film removed is thus directly proportional to time of inhibition, a conclusion confirmed by the figures given above. It is however somewhat singular that the adsorbed gelatine film should acquire a thickness which is directly proportional to the bulk concentration. Iso-electric gelatine is however but sparingly soluble in water and, although the first layer of gelatine may be produced by adsorption, subsequent layers may result as a process of removal of supersaturation by condensation on these layers.

CHAPTER V

THE GAS-SOLID INTERFACE

1. Adsorption.

A gas or vapour brought into contact with a solid will be adsorbed onto the surface to an extent which is dependent on several factors, the nature of the gas and solid, the partial pressure of the adsorbate and the characteristic structure of the solid. This phenomenon of adsorption is however frequently complicated by solution or absorption in the solid to form either solid solutions or compounds. The term sorption has been proposed by McBain to include the two phenomena of absorption and adsorption. Whilst our attention will be chiefly directed to the characteristics of adsorption we shall note that it is frequently difficult to eliminate or to separate the effects due to the other causes.

2. The surfaces of solids.

The difficulties in examination of the properties of a gas-solid interface are enhanced by the fact that in contrast with the gas-liquid interface the surfaces are rarely plane. An attack on the properties of the interface presented by single and uniform facets of crystals is only in the initial stages. In general the solids examined are composite in structure. We may distinguish three separate configurations of solid each of which appears to exhibit characteristic and distinct properties: firstly the uniform surfaces of the crystal facets, secondly macrocapillaries of such a size that in condensation of vapours the Kelvin equation (p. 41) is found to hold, and thirdly microcapillaries or fissures of such small dimensions that the Kelvin equation is no longer applicable. In addition to these structures we may note that the edges of elementary crystal facets, amorphous surfaces, strained and partly disintegrated crystal lattices present a series of forms of extreme complexity.

Crystals.

In order to break the regular space lattice of a crystal a certain amount of energy must be expended, leading to ultimate disintegration to a gas when the energy expenditure is equal to the latent heat of sublimation. The cleavage of a crystal is accompanied by an increase in the surface area and a slight cooling of the crystal surface, and if the work required to separate a crystal of unit cross-section be u the relationship between the change in the total surface energy u and the free surface energy σ is given by the Gibbs-Helmholtz equation

$$\sigma - u = T\frac{d\sigma}{dT}.$$

The fact that the surface atoms in the plane of a crystal lattice surface possess the power of cohesion can also be demonstrated readily by such examples where clean pieces of platinum can be welded together, the joining of optically smooth glass surfaces and the virtual coalescence of clean sheet mica under slight pressure. The cohesive power of the surface atoms of one cleavage plane of a crystal face is not limited to the atoms in the other cleavage face but may be exerted on substances entirely dissimilar to the crystal in composition. Atoms in a crystal may in fact be regarded as surrounded by a field of force, and although there is but little residual attraction within the crystal, where each atom is situated symmetrically as regards the electrical forces of cohesion, the unsaturated character or the intensity of this field assumes large values in the space in juxtaposition to the crystal surface.

The surface of a crystal is thus chemically unsaturated and the existence of a definite surface energy is due to the fact that the surface is unsaturated. Since the surface of a crystal consists of a regular lattice of orderly distributed atoms or ions the surface adhesional forces may be regarded as being distributed over the centres of these atoms (Haber, *J.C.S.I.* XXXIII. 50; *Zeit. f. Elektrochem.* XX. 521, 1914) although in all probability these points represent maxima in a continuous field.

The existence of a surface energy affects both the growth and stability of crystals in equilibrium with their vapour or their saturated solutions*. In the growth of crystals in solution we note not only additional proofs for the existence of a surface energy of solids but that crystals develop those facets such that the interfacial surface energy will, for equal values of the forces of crystallisation, become a minimum. Similar considerations apply to crystals in contact with their vapour, the growth of the surface in which the packing of the atoms or ions produces a minimum value of the surface energy will be favoured, although such free development is frequently modified by such factors as thermal conductivity and diffusion playing a part in limiting the rate of crystal growth.

The problem of the variation in the surface energies of various crystal facets can be attacked from several points of view. Bravais first noted that those planes of a crystal which were most densely packed and were also separated most distantly from the neighbouring parallel plane were those which appeared most frequently in crystals; he noted also that a closely packed surface was usually associated with a wide interplanar distance and *vice versa*. Later Willard Gibbs indicated that the most stable planes on a growing crystal were those possessing the least interfacial surface energy. We thus arrive at a general inference that close packing and a wide interplanar spacing lower the free energy of the surface. Valeton (*Phys. Rev.* XXI. 106, 1920), Niggli (*Zeit. f. anorg. und angew. Chem.* CX. 55, 1920) and Tertsch (*Zeit. f. anorg. Chem.* CXXXVI. 205, 1924) have attempted to correlate the rate of growth of a crystal face with the interplanar spacing. Thus in a face centred cubic crystal of the rock-salt type the interplanar spacings for the 100 : 110 : 111 planes are in the respective ratios $\frac{1}{2} : \frac{\sqrt{2}}{2} : \frac{\sqrt{3}}{4}$, whilst the velocities of growth of the three planes are in the ratio $1 : \sqrt{2} : \sqrt{3}$. The 111 plane growing most rapidly possesses the maximum adhesional surface energy and is thus the least stable, the 100 planes being those which possess the least surface energy and thus appear most frequently. Evidently the surface energies, and thus the growth rates, are not dependent solely on the interplanar distances, but we must ascribe different valencies or adsorptive powers to the planes themselves.

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* The existence of directive forces at heteropolar surfaces is likewise to be inferred from the orientation observed in the crystallisation of sodium chloride on calcite or of potassium chloride on mica, and from the behaviour of liquid crystals on such surfaces.

Tertsch assumes that these stand in the ratio

$$100 : 110 : 111 :: 1 : 1 : 2,$$

thus giving rise to velocities of growth

$$\frac{1}{2} \times 1 : \frac{\sqrt{2}}{2} \times 1 : \frac{\sqrt{3}}{4} \times 2$$

or $1 : \sqrt{2} : \sqrt{3}$, the observed velocities.

Between the alternate $Na^{\cdot}$ and Cl' planes, although the probability of attachment of a Cl' to a $Na^{\cdot}$ plane is twice as great as its probability of attachment to a mixed plane containing both $Na^{\cdot}$ and Cl', in building up several layers the mean probability of growth for such surfaces will be identical with that of a mixed plane.

As justification for this somewhat arbitrary assignment of different degrees of unsaturation or valencies of the ions or atoms in the various planes we may note that any ion in the interior of a face centred cubic crystal may be regarded as the centre of a shell containing six groups of opposite sign round it. An ion in the 100 plane has only five groups of opposite sign round it and requires one more to complete the six which may be regarded as its coordination number, whilst ions in the 110 and 111 planes require two and three ions respectively to complete their sets.

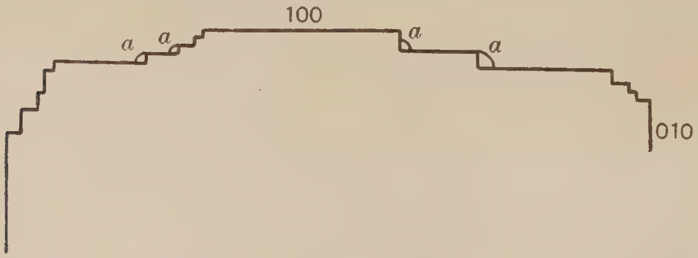
Again we may note that the density of surface packing of atoms or ions in the various planes of a crystal are in the inverse ratio to the interplanar distance, and consequently instead of assuming an increase in attractive power varying as the interplanar distance we may assume that the attractive power falls off as the density of packing of the atoms on the surface increases.

In a face centred cubic crystal of atomic volume V the packing density is given overleaf (Langmuir, *J.A.C.S.* XXXVIII. 2748, 1916).

We have noted however that neither the interplanar spacing nor the packing density of the planes is a sufficient criterion of stability; for, in rock-salt, copper and silver the more open 100 is the most stable facet, whilst in gold and platinum the more closely packed 111 planes are the most stable.

Face	No. per sq. cm.
100	$5{\cdot}56 \times 10^{15}\, V^{-\frac{2}{3}}$
110	$4{\cdot}02 \times 10^{15}\, V^{-\frac{2}{3}}$
111	$6{\cdot}57 \times 10^{15}\, V^{-\frac{2}{3}}$

Not only must we consider the crystal facets themselves from this point of view as differentiated in their respective surface energies but, if we consider the corners and edges common to two crystal surfaces, we note again that the cohesion of atoms so situated in respect to the mother crystal is far weaker than that for atoms actually in one of the surfaces and we should anticipate that the adhesional energy of such atoms, or the external field, will be greater for these edges and corners than for the planes. A crystal undergoing a process of growth or solution will be found to possess a step-like structure. Atoms at the corners of the individual steps (*a a*) are more reactive than atoms in the planes themselves. Thus simple crystals undergoing evaporation or solution will develop the more complicated facets and adsorption on crystals will tend to be greatest on the edges and corners.



The surface energies of simple crystals have been examined from the point of view of the lattice energy of heteropolar compounds by Born (*Atomtheorie des festen Zustands*, 2nd ed. 1923), by Lennard Jones and Taylor (*Proc. Roy. Soc.* A, CII. 496, 1925), *ibid.* and Dent (*ibid.* CXXI. 248, 1928), and Dent (*Phil. Mag.* 7. VIII. 530, 1929).

Salt	NaF	NaCl	KF	KCl
σ, dynes per cm. for 100 plane ...	304	96	180	76·6
$\sigma_{obs.}$ for molten salt	—	66·6	—	69·3

Similar computations have been made for the edge energies of such cubic crystals. Lennard Jones and Taylor (*loc. cit.*) gave the following values:

Salt	Edge energy
NaF	5·13
KF	3·95
NaCl	3·97
KCl	3·06

Agglomerates.

The rapid condensation of a vapour to a solid at low temperatures or the drying of a hydrated oxide results in the formation of an agglomerate of atoms or molecules (Langmuir, *Phys. Rev.* VIII. 149, 1916) which, if possessed of sufficient mobility after condensation, will arrange themselves in crystals possessing a minimum of surface and lattice energy. The mobility of the atoms or molecules is provided by the kinetic energy of thermal agitation and at low temperatures such an agglomerate will be relatively stable. The agglomerate will, as we have noted above, possess a more intense surface field of force and a greater free surface energy than a crystal. It will be more highly unsaturated (Küster, *Lehrbuch d. allg. Physik*, p. 189, 1916; Pawlow, *Zeit. phys. Chem.* LXXXVIII. 316, 1920), exert a higher vapour pressure than the crystalline forms, and exhibit greater powers of adsorption. Substances capable of crystallising in two or more allotropic modifications will likewise possess at all temperatures, with the exception of the transition temperatures, different surface energies, and will consequently exhibit differences in adsorptive powers although smaller in magnitude than in the case considered.

On elevation of the temperature unstable allotropes become converted more rapidly than at low temperatures into the stable modification, and the increased mobility of atoms at high temperatures produces a similar modification in the rapidly cooled conglomerates or amorphous substances; this conversion into the crystalline accompanied by a grain growth or a conversion of the microcrystalline into the macrocrystalline state is termed sintering: the preliminary stage in annealing.

If a high degree of dispersion on a support material be attained not only will there be an extension of the gas-solid interface but the relative area of the irregular or loosely packed and catalytically active surface will be augmented. The high catalytic activity of metals deposited as mirrors on glass (Hinshelwood, Hartley and Topley, *Proc. Roy. Soc.* A, c. 525, 1922) or on silica gel and the protected catalysts utilising gelatine, gum arabic or lysalbinic acid is due to the artificial stabilisation of these reactive patches. Thus "activation" by alternate oxidation and reduction involves two processes, the extension of the gas-solid interfacial area and the disruption of the crystal lattice.

On sintering the surface activity progressively becomes less as is indicated by data on the adsorption of gases and reduction in catalytic activity.

If metals are deposited from vapour on highly cooled surfaces their adsorptive powers are remarkably great, thus we have found that platinum deposited by evaporation on a liquid air cooled glass surface will absorb nitrogen with great facility, the initial quantity adsorbed approximating to the ratio $Pt:N_2::1:1$. A similar great adsorptive power and instability has been observed by Frankenburger and Mayrhofer (*Z. Elektrochem.* xxxv. 590, 1929) in the case of hydrogen by iron deposited by vaporisation. These deposited films sinter readily even at the temperature of melting ice. The sintering or collapse of these finely divided metals is attended with a decreased adsorption capacity for the gas. Frankenburger and Mayrhofer point out that the crystallisation rate as determined by the capacity for adsorbing hydrogen may be greatly reduced by the presence of foreign substances such as sodium chloride.

Unfortunately such data do not permit of calculation of the change in adsorption per sq. cm. caused by the gradual readjustment of the atomic positions into the stable configurations, since during the process of sintering the superficial surface undergoes contraction as well as a modification in structure.

We are indebted chiefly to Smekal (*Ver. Deut. Phys. Ins.* VI. 50, 1925; *Phys. Zeit.* XXVII. 837, 1926; *Ann. phys. Chem.* LXXXIII. 1202, 1927; *Z. Elektrochem.* XXXIV. 477, 1928; *Zeit. f. Physik*, LVI. 1929) for pointing out that, from various properties of an apparently homogeneous crystal (of a metal or salt) such as the hardness, the process of autodiffusion, and the optical and electrical behaviour, it would appear that there exist a number of minute cracks, fissures or grain boundaries of small dimensions. Crystals consist on this view of a mosaic of small blocks. This structure, as pointed out by Zwicky (*Proc. Nat. Acad. Sci.* XV. 253, 816, 1929) (cf. Lennard Jones and Dent, *Proc. Roy. Soc.* A, CXXI. 247, 1928), will extend to the surface for, due to electrostatic forces, the surface of a solid tends to contract and this contraction results in the formation of blocks of a definite average size from 10^{-4} cms. to 100 Å. separated from each other by fissures. The size of the fissure is estimated by Zwicky to be about 100 Å. and some 50 Å. deep. Kapitza (*Proc. Roy. Soc.* A, CXIX. 358, 1928) has likewise presented evidence for the existence of such fissures from the increased conductivity exhibited by apparently perfect crystals of bismuth resulting on compression (cf. Quinney on the behaviour of single and poly crystal iron, *Proc. Roy. Soc.* A, CXXIV. 591, 1929, and Griffith, *Phil. Trans.* A, CCXXI. 163, 1920).

Wyckoff and Crittenden (*J.A.C.S.* XLVII. 2876, 1925) noted from X-ray determinations that iron catalysts prepared by reduction after addition of alumina and potash to the oxide possessed a particle size of 10^{-4} cms. to 100 Å. and that such "promoted" catalysts showed no signs of grain growth on heating to 650° C. for four hours. Feitknecht (*Z. Elekt.* XXXV. 142, 1929) obtained a similar range in particle size for the oxide films formed on copper at 180° C. These experiments go far to confirm the conclusions of Smekal in respect to the mosaic-like or granular structure of solids even when apparently uniformly crystalline.

3. The specific surface of solids.

Since in general solids possess such irregular surfaces as well as cracks and fissures which may be submicroscopic in size, the estimation of the specific surface is a matter of some difficulty. It is clear that, when we consider skeleton growths of atoms and cracks of molecular dimensions, there is a considerable latitude even in the definition of specific surface; it is more correct to speak of accessible surface, denoting the extent of surface which can be reached by the reactant under consideration.

Several different direct methods have been developed for the determination of the accessible surfaces of solids. The simplest in practice consists essentially in determining the initial rate of solution in a soluble reagent of a given mass of the solid and comparing the quantity entering into solution in a given time with the quantity dissolving from a smooth known area of the same material. This method has been employed by Schmidt (*Zeit. physikal. Chem.* CXVIII. 236, 1925) and by Durau (*Zeit. f. Physik*, XXXVII. 419, 1926) and Wolff (*Z. angew. Chem.* XXXV. 138, 1922) for the estimation of the areas of reduced nickel and of powdered glasses. The rates of solution (*vide* p. 283) from different portions of crushed glass and of sintered metals are however by no means uniform and the method cannot be considered as more than semi-quantitative in character.

Paneth and his co-workers (*Zeit. Elektrochem.* XXVIII. 133, 1922; *Zeit. physikal. Chem.* CI. 445, 480, 1922; *Ber.* LVII. 1215, 1924) have shown that the specific surface of relatively insoluble salts such as lead sulphate can be determined with the aid of an isomorphous radio-active salt, e.g. the sulphate of thorium B. If the concentration of a solution of thorium sulphate be determined by electroscopic methods before and after agitation with a known weight of lead sulphate, the ratio of the distribution of thorium ions in solution to those adsorbed by the lead sulphate will be identical with the ratio of lead ions in solution to those present on the solid sulphate surface. By this method the total number of lead ions in the surface of a gram of material may be determined, but the exact evaluation of the area is dependent on assumptions as to the nature of the packing and area of the lead and sulphate ions present in the surface. A modified method for insoluble salts possessing no radioactive isomorph has been elaborated by Hahn and Müller (*Zeit.

Elektrochem. XXIX. 189, 1923; *Ann. d. Chem.* CCCCXL. 121, 1925; *Sitz. Preuss. Akad. Wiss.* XXVI. 535, 1929).

A third method, based upon the observations of Tammann (*Zeit. f. anorg. Chem.* CXI. 78, 1920; CXXIV. 25, 1922) that metals exposed to oxygen or to vapours of the halogens develop brilliant "temper" colours due to Newtonian ring interference caused by the presence of thin films of oxide or halide on the surface, has been developed by Dunn (*Proc. Roy. Soc.* A, CI. 203, 1926) and in some detail by Constable (*Proc. Roy. Soc.* A, CXVII. 376, 1928; CXIX. 196, 1928). The thickness of such an oxide or halide film, if pure, can be determined from a knowledge of the refractive index of the film-forming material and the interference colour observed with the aid of Newton's equation. From a knowledge of the film thickness and either the increase in weight or decrease in electrical conductivity (Constable) of the metal after exposure or the amount of reactive gas taken up by the metal (Dunn) the specific surface may be evaluated. We may observe that the effect of irregularities in the surface of the order of a half wave length of light on the specific surface could not be evaluated with certainty by this method; this would give for a surface of maximum irregularity within these limits an undervaluation of about four times the true specific surface.

We may include amongst the direct methods the work of Bowden and Rideal (*Proc. Roy. Soc.* A, CXX. 63, 1928) on the electrodeposition of hydrogen at metallic surfaces. It was found that the quantity of electricity passed across the interface in order to cause a given increment in cathode potential was the same for liquid electrodes such as mercury, mercury amalgams, gallium and Woods metal but was considerably greater for solid metals. From a measurement of this quantity of electricity it was possible to determine the accessible areas of the metallic surfaces. A few of these are given overleaf.

Wilkins (*Nature*, CXXV. 236, 1930) has likewise pointed out that it should be possible to effect a measurement of the specific surface of solids from the rate of evaporation from the surface or from the rate of surface attack by gases, under the conditions when the rate is proportional to the gas pressure.

Surface	Accessible area per apparent sq. cm.
Solidified alloy ...	1·4
Smooth platinum ...	2·1
Carbon rod	300
Freshly etched silver	51
Aged etched silver ...	37
Sandpapered nickel ...	9·7
Annealed nickel ...	7·7
Rolled nickel ...	3·5
Fresh activated nickel	46
Old activated nickel	29

If the Herz-Knudsen equation is really exactly applicable to condensation of a vapour of a substance on a surface of the material in the solidified form, any difference between the accessible area and apparent area will result in miscalculation of the vapour pressures of solids determined from rates of vaporisation.

The rate of surface attack can be expressed in the form

$$\frac{dx}{dt} = Ane^{-\frac{E}{kT}},$$

where A is the true area of the surface, n the number of collisions per sq. cm. per second which the impinging gas makes with the surface and E the critical energy increment of the surface reaction. From measurement of the velocities of reaction over a range of temperature and a knowledge of n at different pressures both A and E (see p. 251) can be evaluated. Wilkins finds from Langmuir's data (*J.A.C.S.* XXXV. 105, 1913; XXXVII. 1161, 1915) for the oxidation of tungsten wire that the specific surface was 1·2. From the oxidation rate of a platinum wire the specific surface was found to be 22 and for copper which possessed an oxide film on the surface the accessible area was reduced to 1/50 of the apparent surface.

Of the indirect methods employed for the estimation of the specific surface may be mentioned those based upon the hypothesis that surface saturation with an adsorbate is effected when it covers the surface completely with a unimolecular layer. A most exhaustive examination of the surface areas of various forms of charcoal has been made by Paneth and Radu (*Ber.*

LVII. 1221, 1924) who, on the assumption that a saturation maximum is obtained when the surface of charcoal is covered with a unimolecular layer of adsorbate, obtained the following values.

Adsorbate	Animal charcoal		Wood charcoal	
	Mols adsorbed per grm. × 10^{-20}	Surface in sq. metres	Mols adsorbed per grm. × 10^{-20}	Surface in sq. metres
Methylene blue	3·94	220	1·81	101·0
Methyl green	2·56	190	1·26	95·0
Ponceau 2*R*	1·90	119	0·98	56·2
$Pb(NO_3)_2$	6·07	123	2·16	46·2
Acetone	18·50	452	11·00	268·0

Adsorbate	Bone charcoal		Sugar charcoal activated	
	Mols adsorbed per grm. × 10^{-20}	Surface in sq. metres	Mols adsorbed per grm. × 10^{-20}	Surface in sq. metres
Methylene blue	1·14	68·0	0·44	24·8
Methyl green	1·54	114·0	0·26	19·2
Ponceau 2*R*	1·65	103·0	—	—
$Pb(NO_3)_2$	4·50	97·8	0·61	13·2
Acetone	14·70	359·0	2·29	55·9

The high values obtained with acetone were attributed to penetration within the pores of the charcoal.

An interesting series of values for the specific surfaces of various artificial silks was likewise obtained with the aid of methylene blue. The following data indicate the wide variations in specific surface.

Type of silk	Nitro-silk	Cupro-cellulose	Acetic silk
Specific surface	1820	456	28

It is to be noted that the assumption of equality of accessible areas to various adsorbates is not supported even by these data and furthermore the saturation maximum of a semi-colloidal or colloidal dye-stuff is, as we shall note, dependent on its dispersity which in many cases is dependent on the acidity of the solution. In spite of these objections the method is convenient and quick, it gives repeatable results and for comparative purposes, at least, leaves nothing to be desired.

4. Phase discontinuities.

We have noted how the free surface energy of a solid surface may be affected by the atomic or ionic configuration in the surface, the individual facets, edges, corners and unstable agglomerates all possessing different values.

The adsorptive and reactive powers of an atom may be affected not only by juxtaposition of atoms of the same material around it in different configurations and at different distances but also by the juxtaposition of atoms of different materials. Two such cases of "promoter" action may be distinguished. One, which has not been examined in great detail, is observed in cases where the adsorption of two gases by a chemically uniform material affects mutually the strengths of union of the gases to the solid; thus the rate of reaction between hydrogen and liquid sulphur is at a maximum when the surface is covered with both hydrogen and oxygen (Norrish and Rideal, *J.C.S.* CXXIII. 1689, 1923). The other and more important case is obtained when the extraneous or foreign matter is incorporated in the solid. Many chemical reactions are observed to proceed only at the boundary or interface between two solid phases, and consequently in two-dimensional systems only along the line bounding two two-dimensional phases.

Faraday (*Experimental Researches*) observed that a crystal of a hydrated salt placed in a desiccator did not lose water unless a discontinuity in the surface of the crystal was produced by a scratch; efflorescence then proceeded autocatalytically at the ever increasing interface between dehydrated and hydrated salt. We note two points of interest, firstly the increased activity of the scratched or fractured portion, and secondly that of the interface. In addition to the desiccation of salts, as for example hydrates of barium chloride and copper sulphate investigated by Crowther and Coutts (*Proc. Roy. Soc.* A, CVI. 215, 1924) or the removal of combined ammonia in amines, e.g. $CuSO_4$ $5NH_3$ (Predwoditelew and Witt, *Zeit. physikal. Chem.* CXXXII. 47, 1928), a number of chemical reactions in solids proceed at such interfaces. Langmuir (*J.A.C.S.* XXXVIII. 2263, 1916) pointed out that this was probably the case in the decomposition of calcium carbonate, and Centnerszwer and his co-workers (*Zeit. physikal. Chem.* CXI. 79, 1924; CXV. 365, 1925; CXIX. 405, 1926; CXXIII. 127, 1926; *J.P.C.* XXIX. 733, 1925) (see also Brazs, *Zeit. physikal. Chem.* CXLVII. 3, 1929) have examined the decomposition of several other carbonates from this point of view. The decomposition of silver oxide (Lewis, *Zeit. physikal. Chem.* LII. 310, 1905), silver oxalate (Macdonald and Hinshelwood, *J.C.S.* CXXVII. 2764, 1925), potassium hydrogen oxalate (Hume and Colvin, *Proc. Roy. Soc.* A, CXXV. 636, 1929), permanganates (Sieverts and Theberath, *Zeit. physikal. Chem.* C. 403, 1922; Rojinsky and Schulz, *ibid.* CXXXVIII. 21, 1928) may likewise be cited as examples of such reactions in solids.

Cases of physical change at solid-solid interfaces are quite common, the monoclinic rhombic sulphur conversion (Frankel and Goetz, *Zeit. anorg. Chem.* CXLIV. 45, 1925; Hume and Colvin, *Phil. Mag.* VIII. 590, 1929) and the allotropic transformation of yellow mercuric iodide (Kohlschütter, *Koll. Zeit.* XLII. 254, 1927) are representative of well-known examples. Since the decomposition of such solids as calcium carbonate proceeds only at the $CaCO_3/CaO$ interface it is necessary to suppose that the reverse reaction, namely the reaction between calcium oxide and carbon dioxide, likewise follows the same course. Such chemical actions between a gas and a solid, important in many cases of heterogeneous catalysis, have been established, such as the reduction of copper oxide by hydrogen by Pease and Taylor (*J.A.C.S.* XLIII. 2179, 1921; XLIV. 1637, 1922; see also Larson and Smith, *J.A.C.S.* XLVII. 346, 1925; Okayama, *Zeit. Elektrochem.* XXXIV. 294, 1928) which proceeds only at the CuO/Cu interface. The reduction of nickel oxide by hydrogen according to Hughes and Bevan (*Proc. Roy. Soc.* A, CXVII. 101, 1928) follows a similar course. The formation of the nitrides of lithium (Frankenburger, *Zeit. Elektrochem.* XXXII. 481, 1926) and calcium (Antropoff and Germann, *Zeit. physikal. Chem.* CXXXVII. 209, 1928) can be cited as reactions of a similar type.

A true case of two-dimensional reaction at an interface on the boundary between two two-dimensional phases, which presents some analogy to the case of the interaction of hydrogen and sulphur cited above, is the investigation of Adhikari and Felman (*Zeit. physikal. Chem.* CXXXI. 347, 1927) on the interaction of mercury and iodine which takes place only at the HgI_2/adsorbed I_2 interface.

The catalytic decomposition of hydrogen peroxide likewise only occurs at certain interfaces such as Hg/HgO (Antropoff, *Zeit. physikal. Chem.* LXII. 567, 1908) or Ag/Ag_2O (Wright, *Trans. Farad. Soc.* XXIX. 539, 1928).

We have noted that Faraday's experiment established two separate facts, the commencement of the reaction at a broken edge and the subsequent interfacial reaction. Since in all these reactions one phase may be always regarded as metastable the reaction at the interface may be attributed to the presence of nuclei necessary for the removal of the metastability, a point of view suggested by Ostwald; on this view there is no necessity to assume any modification in the free energies of either phase at the interphase to account for the fact that the seat of reaction is confined to this area.

That some modification in the field does however take place at such interfaces is seen most readily in the results of investigations on the effect of promoters in catalytic actions.

5. The Freundlich isotherm.

The failure of the simple partition law of Henry, $x = kp$, to express the distribution of a gas between the surface phase and the space above it led Freundlich to propose an empiric isotherm which within limits at least gives a fair agreement between experimental data and those calculated with its aid. This equation is generally expressed in the form

$$\frac{x}{m} = ap^{\frac{1}{n}},$$

where x is amount of gas adsorbed per m grm. of adsorbent under a gas pressure p, and a and n are arbitrary constants.

The value of a is dependent on the units employed for measurement, whilst n is a characteristic not only of the adsorbing agent but also of the adsorbate. Thus at 20° C. the approximate values of $\frac{1}{n}$ for a few easily liquefiable gases are as follows:

Gas	$\frac{1}{n}$ for charcoal	$\frac{1}{n}$ for glass
CO_2	0·394	0·66
NH_3	0·437	0·53
SO_2	0·324	0·28
$CHCl_3$	0·122	—
N_2O	—	0·49

The two arbitrary constants likewise vary with the temperature and we note as significant not only that $1/n$ approaches unity as the temperature is elevated but also it is in reality not a constant over a wide range since it increases as the gas pressure is reduced.

Chappuis (*Wied. Ann.* XIX. 29, 1883) obtained a value of $\frac{1}{n} = 0{\cdot}84$ for the adsorption of ammonia by charcoal at pressures between 3–5 mm., whilst from Travers' (*loc. cit.*) data on the adsorption of carbon dioxide by charcoal the following variations may be noted:

Temp. °C.	a	$\frac{1}{n}$
– 78	14·290	0·133
0	2·960	0·333
35	1·236	0·461
61	0·721	0·479
100	0·324	0·518

Accurate plotting of the experimental data in the logarithmic form

$$n \log \frac{x}{m} = nA + \log p$$

reveals the fact that in no case does a linear relationship obtain, provided that the adsorption is determined over a sufficiently extensive range of pressures. This departure from the Freundlich equation is most marked at extremely low pressures and not inconsiderable at high pressures. Although the Freundlich isotherm possesses two variables permitting of a considerable latitude in adjustment, yet the data almost always reveal an increasing value for $\frac{1}{n}$ as the pressure is reduced.

The data of Magnus (*Zeit. anorg. Chem.* CL. 311, 1926; CLV. 205, 220, 1926; CLXXIV. 142, 1928), Richardson (*J.A.C.S.* XXXIX. 1828, 1917; XLV. 2638, 1923), Titoff (*Zeit. physikal. Chem.* LXXIV. 641, 1910), Travers (*Proc. Roy. Soc.* A, LXXVIII. 9, 1907) may be cited as examples of careful investigation as to the adequacy of the Freundlich adsorption isotherm.

This equation can readily be deduced from the Gibbs adsorption isotherm on the assumption that the change in free surface energy on adsorption of a gas is at all times proportional to the change in the amount of gas adsorbed and to the absolute temperature, or

$$d\sigma = -nRTdx \quad \dots\dots\dots\dots\dots\dots\dots(1).$$

If in the Gibbs equation

$$\Gamma = -\frac{d\sigma}{d\mu} = -\frac{d\sigma}{RTd\log p}$$

we replace Γ by x the amount adsorbed per sq. cm. and also $d\sigma$ by $-nRTdx$ from (1), we obtain

$$x = \frac{nRTdx}{RTd\log p} \dots\dots\dots\dots\dots\dots\dots\dots(2),$$

or

$$x^n = kp,$$

which is the Freundlich expression. In films on liquid surfaces this assumption of a proportionality between the lowering of the surface tension and the surface concentration, i.e. of

$$d\sigma = -nRTd\Gamma \text{ or } FA = nRT,$$

is, as we have observed, not true except at extremely great dilutions, where n becomes equal to unity.

It is also evident that according to this equation there is no saturation maximum for a definite area of adsorbing surface. Indefinite increase of the pressure produces indefinitely large adsorption. The experimental data indicate in a perfectly definite manner that in many cases an adsorption maximum or surface saturation is obtained. Arrhenius (*Medd. Nobel Inst.* II. 7, 1911) was the first to introduce the concept of a definite saturation value (s) which varied with the nature of the adsorbing agent and with the adsorbate. On the hypothesis that the amount taken up for a small alteration of the pressure depended on the relative extent of surface saturation already obtaining, Arrhenius showed that the p, x curves could be expressed in the form

$$k\frac{dx}{dp} = \frac{s-x}{x},$$

or

$$\log_{10}\frac{s}{s-x} = 0{\cdot}4343\,\frac{x}{s} - \frac{0{\cdot}4343}{ks}\,p.$$

The equation is thus superior to that of Freundlich in that the existence of a surface saturation is realised as well as a physical significance given to one of the constants.

The following values represent the surface saturation constant s for charcoal in c.c. at N.T.P. per grm. together with the a constant of the Van der Waals' equation for the respective gases.

Gas	s in c.c. at N.T.P. per grm.	$a \times 10^3$
He	0·227	0·42
Ar	1·67	2·59
N_2	2·35	2·68
O_2	2·50	2·69
CO	3·20	2·80
CH_4	9·4	3·67
CO_2	30·4	7·01
NH_3	71	8·08
C_2H_4	41	8·83

Although there is some experimental justification for the conception of a saturation concentration, yet this equation containing but one variable was found by Schmidt to conform to the experimental results but very indifferently. Schmidt (*Zeit. physical. Chem.* LXXVIII. 667, 1912) made the additional hypothesis that the adsorption coefficient k decreases in magnitude with the amount of gas adsorbed in an exponential manner, or

$$k = k_0 e^{-Ax},$$

where A is a constant, obtaining thus the equation

$$\frac{dx}{dp} = k_0 (s - x) e^{-Ax} \quad \text{or} \quad ln \frac{s}{s - x} - Ax = Kp,$$

an equation somewhat similar in form to that proposed by Arrhenius. That these equations do not, in actuality, express the adsorption isotherm over very wide ranges of pressure can be seen from the following values of k calculated with the aid of the Arrhenius equation from the experimental data of Titoff and Homfray:

CO_2 on charcoal at 0° C.		C_2H_4 on charcoal at 0° C.	
p	k	p	k
0·05	24·9	7·00	12·3
0·32	159·0	4·00	13·2
1·09	89·0	2·28	11·3
2·54	60·5	1·70	11·2
8·30	52·0	0·87	11·6
17·35	48·9	0·54	10·4
31·59	52·7	0·15	11·3
45·72	56·0		
58·91	58·9		
70·32	61·6		
75·51	62·2		

The realisation that the Freundlich equation was not generally applicable and gave no insight into the mechanism of adsorption or the state in the adsorbed layer has led to numerous attempts to formulate more exact equations. These developments may be said, in general, to have followed two broad lines either in a detailed investigation of the molecular processes operative at a gas-solid interface or thermodynamical considerations amplified by the supposition of the operation of different types of electrical forces at the interface.

We will consider briefly the investigations which have justified these two methods of approach.

6. The reflection and condensation of molecules on surfaces.

The adsorption isotherm for a gas on a solid surface represents the conditions of equilibrium attained for equal velocities of two opposing processes, those of condensation and of evaporation. A consideration of the process of condensation clearly involves a number of important questions, whether, for example, all molecules suffer specular reflection at the surface or whether they are condensed and re-evaporated at random, whether there is any relationship between the direction of incidence and of evaporation and what proportion of its energy and momentum an impinging molecule gives to the surface. Equally important are the determinations of the duration of life of a molecule adsorbed on a surface and an answer to the question whether molecules adsorbed on a surface can during their lifetime on that surface undergo any change of position, i.e. do they behave as two-dimensional gases or liquids or is the system rigid in these dimensions?

An attack on these problems was made first by Knudsen (*Ann. der Phys.* XXVIII. 75, 1908; XXXV. 389, 1911) by investigating the thermal conductivity and flow of gases at low pressures. Evaluation of the accommodation coefficient of gases, this coefficient being the ratio of the heat actually carried away by impinging and reflected molecules to that which would have been carried away if thermal equilibrium had been attained*, revealed in general high values, the lowest value being 0·26 for hydrogen on polished platinum and glass. Only in the case of hydrogen and helium were values less than 0·8 obtained.

Measurements of a similar kind undertaken by Langmuir (*J.A.C.S.* XXXVII. 425, 1915) revealed that the accommodation coefficient was independent of the nature of the solid surface provided that it was polished, a result taken by Langmuir to indicate that under the conditions of the experiments the surfaces were covered with a layer of adsorbed gas. Knudsen (*Ann. der Phys.* XXVIII. 75, 1908) showed that the hypothesis of a completely irregular reflection led to a good agreement between the theoretical and experimental values for the rate of flow of rarefied gases through tubes.

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* The difference between the accommodation coefficients of hydrogen on metals and metallic oxides has been used by Hughes and Bevan (*Proc. Roy. Soc.* A, CXVII. 100, 1927) and Chapman and Hall (*ibid.* CXXIV. 478, 1929) to show that in the combination of hydrogen and oxygen at nickel and silver surfaces the metals are actually covered with an oxide film. In addition to the thermal accommodation coefficient, we note that condensation coefficient, reaction coefficient, reflection coefficient and Maxwell's specular reflection coefficient have been employed somewhat indiscriminately by various investigators.

Further information on these points is gained from a study of the properties of streams of molecules at low pressures or of molecular rays. The early investigations of R. W. Wood (*Phil. Mag.* XXX. 300, 1915) and of Knudsen (*Ann. der Phys.* L. 472, 1916) showed that the rate of condensation of the molecules constituting such a stream was markedly dependent on the temperature of the condensing surface, and that there existed a critical temperature which separated a region of very rapid condensation from one of very slow condensation. A few of their data for glass surfaces are appended in the following table.

Beam	Critical temperature ° C.	Observer
Mercury	− 140	W.
	− 140 to − 130	K.
Cadmium	− 90	W.
Zinc, cadmium, magnesium	− 183 to − 78	K.
Iodine	− 60	W.
Copper	+ 350 to 575	K.

Wood also investigated the direction of reflection of mercury from a glass surface and found that the number of molecules evaporating in a given direction was independent of the direction of the incident beam. The number was likewise found to vary as the cosine of the angle made with the normal to the surface by Knudsen (*Ann. der Phys.* XLVIII. 1115, 1915) with the aid of an ingenious geometrical arrangement.

Langmuir (*Proc. Nat. Acad. Sci.* 141, 1917) showed that in the case of the condensation of cadmium on glass the temperature at which condensation commenced depended on the density of the molecular stream striking the glass, a stream of high density impinging for a short time interval was found to be more effective than a stream of low density impinging for prolonged periods.

These experiments indicated that the simple hypothesis of the alternatives of reflection or of condensation was not tenable and suggested the possibility of the formation of relatively stable groups or nuclei. Langmuir established the existence of such nuclei possessing a relatively long life on the surface by sensitising part of a surface with cadmium, raising the temperature so that all single atoms of cadmium would evaporate and then obtaining a deposit on the previously sensitised surface. The simplest type of nucleus consists of a doublet or pair of atoms, and the assumption is made that such a doublet, the formation of which is facilitated by the surface motion of the adsorbed atoms, possesses a life much longer than that of a single atom on the surface. We can with Frenkel (*Zeit. f. Physik*, XXVI. 117, 1924) evaluate the relationship between the critical temperature and stream density in the following manner.

Let n be the number of atoms adsorbed per sq. cm., σ the area of the force field of an adsorbed atom which permits the capture of another atom to form a doublet, and σ_0 the target area of the adsorbed atom according to the kinetic theory. Frenkel first assumes that the area of the force field is related to the target area by an expression of the type

$$\sigma = \sigma_0 e^{\frac{\Delta u}{kT}},$$

where Δu is the energy of dissociation of a doublet.

The number of single atoms on the surface will be

$$n_0 = n\,(1 - n\sigma)$$

and of paired atoms $\qquad n_1 = n^2\sigma.$

If the molecular beam density be such that ν atoms strike unit area per second the rate of surface adsorption will be

$$\frac{dn}{dt} = \nu - \alpha n_0 - \alpha' n_1 = \nu - \alpha n + \beta n^2,$$

where $\alpha = \frac{1}{\tau}$ and $\alpha' = \frac{1}{\tau'}$, τ and τ' being the lives of the single molecules and doublets respectively on the surface and

$$\beta = (\alpha - \alpha')\,\sigma_0 e^{\frac{\Delta u}{kT}}.$$

At equilibrium the rates of condensation and of evaporation of single atoms and of doublets must be equal or

$$\frac{dn}{dt} = 0.$$

Hence $$\nu - \alpha n + \beta n^2 = 0$$

or $$n = \frac{\alpha \pm \sqrt{\alpha^2 - 4\beta\nu}}{2\beta}.$$

When $\alpha^2 \geqq 4\beta\nu$, n must be real, the other root being physically impossible, i.e. there is a critical value of ν, or $\nu_c = \frac{\alpha^2}{4\beta}$ is necessary before a dense metallic condensate can be formed.

If the mean life of an isolated atom τ be related to the oscillation frequency of the lattice τ_0 and its energy of adsorption u by the expression

$$\tau = \tau_0 e^{\frac{u}{kT}},$$

and for an atom in a doublet

$$\tau_1 = \tau_0 e^{\frac{u+\Delta u}{kT}} = \tau_0 e^{\frac{u_1}{kT}},$$

then ν_c the critical stream density is equal to

$$\frac{1}{4\sigma_0 \tau_0} e^{\frac{u_1}{kT}}.$$

We may note that if it be assumed that it takes several atoms, e.g. four, to form a nucleus instead of two as assumed by Frenkel, we obtain a similar expression for the critical stream density, for from the equation

$$\frac{dn}{dt} = \nu - \alpha n + \beta n^4,$$

where $$\alpha = \frac{1}{\tau} \text{ and } \beta = \left(\frac{1}{\tau} - \frac{1}{\tau'}\right)\frac{\sigma_0{}^3 e^{\frac{3\Delta u}{kT}}}{3\,!},$$

we obtain a minimum value for $\frac{dn}{dt}$ when $\alpha = 4\beta n^3$ or $\frac{3}{4}\alpha n = \nu_c$ or $\nu_c = \frac{A}{\sigma_0 \tau_0} e^{\frac{u_1}{kT}}$, a form similar to that obtained by Frenkel.

If the nucleus be large the value of Δu, the energy required to separate an atom from the nucleus, should evidently approach the latent heat of sublimation of the adsorbed material.

Whilst qualitatively the existence of a critical temperature for condensation dependent on the stream density of the molecular ray confirms the hypothesis of Frenkel, the quantitative aspects of the condensation process are at present by no means so satisfactory.

Wertenstein (*J. de Physique*, IV. 281, 1923) observed that on heating a drop of mercury in a vessel to 22° C., two degrees higher than the walls of the vessel, the pressure first rose to the equilibrium pressure at 22° C. and then fell over a period of three hours to the equilibrium value obtaining for the wall temperature. He also found that when no liquid mercury was present equilibrium of adsorption was obtained in ten minutes, these periods representing the time necessary to form nuclei and to effect condensation. With a stream density of $\nu = 10^{17}$ atoms per sq. cm. per sec. at 22° C. the value of the mean lives of the single atoms of mercury on the glass surface are found to be

T° K.	τ mean life in secs.
295	$1{\cdot}08 \times 10^{-5}$
308	$6{\cdot}78 \times 10^{-6}$
339	$1{\cdot}8 \times 10^{-6}$

On application of Frenkel's expression

$$\tau = \tau_0 e^{\frac{u}{kT}},$$

we obtain $u = 4900$ cals. per mol and > 9000 cals. per mol respectively for the two cases, a poor agreement.

Chariton and Semenoff (*Zeit. f. Phys.* XXV. 287, 1924) measured the critical temperatures and stream densities for the condensation of cadmium on picein, obtaining

$T = 203°$ K. $\nu = 2 \,.\, 10^{17}$ atoms per sq. cm. per sec.
$T = 198°$ K. $\nu = 1 \,.\, 10^{17}$,, ,,

whence $u + \Delta u = u_1 = k \dfrac{T_1 T_2}{T_1 - T_2} \log \dfrac{\nu_1}{\nu_2} = 11{,}000$ cals. per grm. mol and $\sigma_0 \tau_0 = 1{\cdot}6 \,.\, 10^{-30}$. Taking $\sigma_0 = 3 \,.\, 10^{-15}$ cm.^{2} we obtain $\tau_0 = 5 \,.\, 10^{-16}$ secs., an oscillation frequency much smaller than that anticipated for the oscillation of an atom in a lattice, that in a cadmium lattice being *ca.* $4 \,.\, 10^{-13}$ secs.

If the energy of dissociation of a cadmium doublet bears the same relationship to the latent heat of sublimation of cadmium as the energy of dissociation of Hg_2 (6370 cals.) does to the latent heat of evaporation of mercury (155,000 cals.) we obtain $\Delta u = 2400$ cals. per grm. mol for the dissociation of the cadmium pairs and an energy of evaporation of single cadmium atoms of $u = 11{,}000 - 2400 = 8600$ cals. per grm. mol, whence we obtain

$T°$ K.	τ mean life in secs.
150	$1{\cdot}65 \times 10^{-3}$
200	$1{\cdot}25 \times 10^{-6}$
250	$1{\cdot}7 \times 10^{-8}$

From Estermann's experiments for the condensation of cadmium (*Zeit. Elektrochem.* XXXI. 442, 1925) on the other hand we obtain

Surface	Energy of condensation cals. per mol
Copper	3000
Silver	5000
Glass	3500
Mercury on silver	2500

If we assume the correctness of the previous value for the dissociation of cadmium doublets on glass, i.e. $\Delta u = 2400$ cals. per grm. mol, we obtain $\tau_0 = 5 \,.\, 10^{-5}$ secs. and

$T°$ K.	τ mean life in secs.
150	2×10^{-3}
200	$7{\cdot}5 \times 10^{-4}$
250	$4{\cdot}5 \times 10^{-4}$

These values are of quite a different order to those obtained by Chariton and Semenoff, whilst the energy of evaporation of mercury on glass is much lower than that computed from Wertenstein's experiments.

A comparison of the values of condensation of β recoil atoms from Thorium B and of Radium C obtained by Duat and Phillip

(*Z. Physik*, LIX. 6, 1929) and by Wertenstein (*C. R.* CLXXXVIII. 1045, 1929) indicates the greater ease of condensation of atoms on an isotopic receiver on which nucleus formation is readily obtained.

Cockcroft (*Proc. Roy. Soc.* A, CXIX. 1928) examined the condensation of cadmium over a wide range of stream densities (ν varying over one thousand-fold). He showed in general that the Frenkel relationship between temperature of condensation and stream density was valid and computed a value of $u_1 = 5{,}680$ cals. per grm. mol, an approximate value of $\Delta u = 2{,}000$ cals. per grm. mol and $\tau_0 = 2{\cdot}6 \;.\; 10^{-9}$ secs. Assuming that the correct value of Δu was 2,400 cals. per grm. mol he obtained

$T°$ K.	τ mean life in secs.
150	$1{\cdot}43 \times 10^{-4}$
200	$9{\cdot}6 \times 10^{-6}$
250	$1{\cdot}85 \times 10^{-6}$

The critical density was again found to be independent of the nature of the condensing surface, but on taking precautions to remove any gas film present he obtained qualitative indications of large changes in the critical density with different surfaces. We note that the presence of gas films on the condensing surface is the chief factor in causing the discrepancies between the values obtained by these different investigators, and a re-investigation under conditions of high vacuum with freshly formed condensing surfaces is clearly desirable.

Clausing (*Diss. Leiden*) has attempted to evaluate the mean life of condensed cadmium atoms by allowing the ray to impinge through a diaphragm slit on to a rotating wheel, from which after being carried for a distance the molecules re-evaporated and were collected on a condensing surface close to the wheel. Although in these experiments the necessary correction due to the momentum carried by the evaporating molecules was large, this ingenious method would appear capable of development.

The specular reflection of beams from crystal and metallic surfaces has, with the advent of the concept of the wave character of molecular beams, received renewed attention; thus Elliott and Olsen (*Phys. Rev.* XXXI. 643, 1928; XXXIV. 493, 1929) have obtained specular reflection of cadmium and mercury on sodium chloride surfaces (see also Knauer and Stern, *Zeit. f. Physik*, LIII. 779, 1929).

7. The Langmuir isotherm.

The conclusion that the process of molecular reflection at a surface involved condensation and re-evaporation and that the surface of a solid could be regarded as a space lattice of elementary atoms, each elementary vacant space above or between each atom being the possible home of a condensed gas molecule, led Langmuir (*Phys. Rev.* VIII. 149, 1916; *Proc. Nat. Acad. Sci.* III. 141, 1917; *J.A.C.S.* XL. 1360, 1918) to develop an isotherm based upon the view that under conditions of equilibrium the rates of condensation and re-evaporation were equal.

The rate of effusion of a gas from an orifice has been shown by Herz and Knudsen to be given by the equation

$$\nu = 43{\cdot}75 \times 10^{-6} \frac{p}{\sqrt{MT}} = \frac{\kappa p}{\sqrt{MT}},$$

where ν grm. mols effuse per sq. cm. of orifice per second,

p is the gas pressure in bars (10^6 bars = 1 atmosphere),
M is the molecular weight of the gas,
T the temperature in ° K.

Since the coefficient of accommodation α at most surfaces is almost unity a gas striking a surface may be regarded as effusing into a vacuum.

If the surface be partly covered with the gas the impinging molecules will strike and adhere to the vacant portions.

At equilibrium a fraction θ' of the surface will be covered with adsorbed gas and a fraction θ will still be bare.

We thus obtain $\theta + \theta' = 1$.

The rate of condensation of the gas on the uncovered portions of the surface will be $\alpha\nu\theta$, whilst the rate of evaporation from the covered area will be $\frac{\theta'}{\tau}$, where $\frac{1}{\tau}$ is the rate of evaporation from unit area. At equilibrium the rates of condensation and evaporation will be equal, or

$$\frac{\theta'}{\tau} = \alpha\nu\theta. \quad \therefore \theta' = \frac{\alpha\tau\nu}{1 + \alpha\tau\nu}.$$

If x grm. mols are adsorbed per unit area then $\theta' = \frac{N}{N_1} x$, where N is the number of elementary spaces per sq. cm. of surface and N_1 Avogadro's number ($6{\cdot}065 \times 10^{23}$ molecules per grm. mol).

Hence $$x = \frac{N_1}{N} \frac{\alpha\tau\nu}{(1 + \alpha\tau\nu)} = \frac{abp}{1 + ap},$$

since $\nu = kp$, which is Langmuir's equation for the adsorption isotherm, where a and b are constants, a being proportional to the length of life of the adsorbed molecule on the surface. At very low pressures where ap is small compared with unity we obtain

$$x = abp,$$

or the amount adsorbed is proportional to the gas pressure (Williams, *Proc. Roy. Soc. Edin.* XXXIX. 48, 1919; Chaplin, *Proc. Roy. Soc.* A, CXXI. 344, 1928; Kälberer and Mark, *Zeit. physikal. Chem.* CXXXIX. 151, 1928). At very high pressures we obtain $x = b$ or a definite saturation maximum is obtained.

In developing an adsorption isotherm for gases on solid surfaces Frenkel (*Zeit. f. Physik*, XXVI. 117, 1924) assumes that lateral adhesion to form doublets does not occur and the processes of condensation and evaporation proceed as imagined by Langmuir.

If there be n molecules each of effective area σ_0 per unit area, then of ν molecules striking and condensing on this area per second only $\nu(1 - n\sigma_0)$ will be able to adhere. If the average length of life be τ then, equating the rates of condensation and evaporation, we obtain

$$\frac{n}{\tau} = \nu(1 - n\sigma_0).$$

Inserting the value $\tau = \tau_0 e^{\frac{u}{kT}}$ and $\nu = \frac{\kappa p}{\sqrt{MT}}$ we obtain

$$n = \frac{\frac{\kappa p}{\sqrt{MT}} \tau_0 e^{\frac{u}{kT}}}{1 + \sigma_0 \tau_0 e^{\frac{u}{kT}} \frac{\kappa p}{\sqrt{MT}}} \text{ or } x = \frac{abp}{1 + ap},$$

a form identical with that derived by Langmuir.

We may note that if the characteristics of the surface phase be expressed by $F(A - B) = F\left(\frac{1}{x} - B\right) = RT$ and the Gibbs equation in the form

$$\frac{x}{1 - xB} = -\frac{c}{RT}\frac{dF}{dc},$$

we obtain on eliminating F

$$\frac{dc}{c} = \frac{dx}{x(1 - xB)}, \quad \text{or} \quad c = \frac{\kappa x}{1 - xB},$$

the adsorption isotherm of Langmuir. With the more general equation of state (see p. 64)

$$F(A - B) = F\left(\frac{1}{x} - B\right) = iRT,$$

and the Gibbs equation in the form given above, we obtain

$$\frac{x}{1 - xB} = Kc^{\frac{1}{i}},$$

an equation similar to that of Freundlich when the surface saturation is small.

The Langmuir isotherm has been tested not only by Langmuir but by numerous other investigators and has been shown to be applicable in a great number of cases. The premises on which it rests involve certain assumptions which are by no means self-evident. In the first place it is assumed that the surface may be regarded as perfectly homogeneous; experimental evidence against this assumption is convincing and both Langmuir and others, including Pease (*J.A.C.S.* XLV. 1290, 1923) and Constable, have pointed out that for ordinary non-uniform materials the composite surface may be regarded as made up of uniform areas on each of which an isotherm with a suitable value of τ, the mean life on the respective surface, is applicable. The summation represents the total adsorption

$$x = \Sigma \frac{abp}{1 + ap}.$$

Pease (see also Foresti, *Gaz. Chim. Ital.* LIX. 282, 1929) considers that these areas may for all practical purposes be divided into three, each possessing a characteristic life, one very long and one very short, thus giving an equation in the form

$$x = b_1 + \frac{a_2 b_2 p}{1 + a_2 p} + a_3 b_3 p = \frac{b_1 + mp + np^2}{1 + a_2 p},$$

an equation which is somewhat unsatisfactory owing to the large number of arbitrary constants involved; whilst Constable (*Proc. Camb. Phil. Soc.* XXII. 738, 1925; XXIII. 172, 593, 1926) suggests that the surface atoms, neglecting the orientating effects of the forces of crystallisation, are so distributed as to present a continuous series of small patches each of different adsorbing powers, their number and the lives of adsorbed molecules thereon being distributed according to the probability law. This assumption leads to the somewhat complex equation

$$x = \frac{N_1}{N} \int \frac{\tau \mu \, db}{1 + \tau \mu}, \quad \text{where} \quad b = \kappa \tau^2 e^{-\tau^2}.$$

The second assumption involved in the Langmuir isotherm is that an adsorbed molecule exerts no other effect on the surface than that of a covering action on the one or two elementary squares of the space lattice which it occupies. We have already noted that in the case of the condensation of metallic vapours in building up aggregates longer lives are found for doublets than for single atoms and that the apparent range of action of an adsorbed metallic atom may be as great as thirty or more times the molecular area. It is necessary to examine how far such extended range of action may be due to the adsorbate behaving as a two-dimensional fluid possessed of mobility rather than as a frozen solid.

8. On the surface mobility of adsorbed molecules.

It has been noted that Frenkel's hypothesis assumes that the range of attraction of an adsorbed atom is greater than that presented by its kinetic target area and is related to the energy of doublet dissociation by an expression of the type

$$\sigma = \sigma_0 e^{\frac{\Delta u}{kT}},$$

and that the experimental data cited lead to values of this range of attraction which are of the order of thirty times that of the actual molecular area. The formation of doublets would thus be materially assisted by a lateral movement of the adsorbed molecules over the surface of the condensing solid. Independent experimental evidence for such superficial mobility on solid surfaces has been provided by Volmer and his co-workers.

Volmer and Estermann (*Zeit. f. Physik*, VII. 13, 1921) examined the rate of growth of minute crystals of mercury formed in a closed space above liquid mercury maintained at − 10° C., the space above the liquid being cooled below this temperature by means of an inverted cooler kept at − 63° C. After a few minutes small and extraordinarily thin hexagonal crystals were obtained in the gas space. Microscopic measurements indicated that the crystal diameter was some 10^4 times the crystal thickness and it was found that the diameter grew at the rate of some $3 \, . \, 10^{-2}$ cms. per minute.

The maximum rate of growth of a crystal face by condensation of the mercury vapour can be determined with the aid of the Herz-Knudsen equation

$$v = \frac{\alpha}{\Delta} \sqrt{\frac{M}{2\pi RT}}\, p,$$

where α is the condensation coefficient, Δ the density and p the vapour pressure of the mercury. Inserting the values $p_{-10^\circ \mathrm{C}} = 8{\cdot}7 \, . \, 10^{-2}$ dynes per sq. cm. and $\alpha = 1$ we obtain a maximum value for $v = 2{\cdot}5 \, . \, 10^{-7}$ cms./sec. or, since the crystal has two sides, a maximum rate of $3 \, . \, 10^{-5}$ cms./minute. The observed crystal growth rate is thus nearly a thousand times the maximum theoretically obtainable by direct condensation on the surface. This result is most readily explicable on the hypothesis that molecules adsorbed on the surface may not only re-evaporate or commence the formation of new nuclei but may likewise move over the surface which is one of equipotential until they become anchored at the edges of the minute crystal. Volmer and Adhikari (*Zeit. f. Physik*, XXXV. 170, 1925) re-investigated a phenomenon observed by Lehmann (*Molekularphysik*, II. 344, 1888) that a liquid melt of needle crystallising material frequently sets to a star, the needles of which project above the original free surface of the melt. These projections may be as long as 0·1 mm. in the case of benzophenone. On the assumption that there exist adsorbed but mobile molecules of benzophenone on the crystal facets this feature of the growth is similar to that noted in the case of the crystals of mercury. Volmer and Adhikari showed the existence of this surface diffusion process by removing benzophenone from the end of a crystal with the aid of mercury drops; by suitable adjustment, only the benzophenone supplied by lateral diffusion over the surface of a small needle of benzophenone could be removed. These experiments were extended (*Zeit. f. Physik*, XXXIX. 46, 1926) to the removal of benzophenone by dropping mercury after lateral migration over the surface of a small crystal and across a glass edge interposed between the benzophenone and the mercury stream.

Moll (*Zeit. physikal. Chem.* CXXXVI. 183, 1928), utilising Volmer's method, has observed surface diffusion for phthalic anhydride, coumarin and diphenylamine, but paraffin and cetyl alcohol gave negative results.

The development of metallic films deposited by molecular beams has been described by Estermann and Stern (*Zeit. physikal. Chem.* CVI. 397, 1923), who showed that films of calculated thickness 0·2 Å. could be rendered visible.

Evidence for the two-dimensional mobility for mercury atoms condensing on silver has been presented by Knauer and Stern (*Zeit. f. Physik*, XXXIX. 774, 1926) and by Cockcroft (*Proc. Roy. Soc.* A, CXIX. 1928), who showed that cadmium atoms could diffuse and condense on cadmium sensitised copper in places protected from the direct impact of a molecular beam of cadmium atoms.

Estermann (*Zeit. phys. Chem.* CVI. 403, 1923; *Zeit. Physik*, XXXIII. 320, 1925) has likewise observed both the growth of silver crystals and of cadmium deposited by molecular rays due to lateral mobility.

In a different direction Hevesey and Obrutscheva (*Nature* CXV. 674, 1925) indicate that radioactive indicators may be employed in experiments on auto-diffusion through metals to show that migration takes place at greatest speed over the surface of the metals between slip planes, or in the cracks shown to exist by Smekal and Joffé.

Becker (*Trans. Amer. Electrochem. Soc.* May 1929) has also presented evidence for the existence of such surface migration for caesium, barium and oxygen atoms on tungsten in a very ingenious and definite manner. The electron work function of tungsten is lowered by the presence of barium and caesium and raised by oxygen. If the thermionic emission from the two sides of a hot strip of tungsten be measured and a film of barium be deposited on one side so as to give approximately half an atomic layer, the emission from the covered side will greatly exceed that from the bare one which is at the same temperature. At temperatures above 900° K. it is found that the emission from the coated side gradually sinks whilst that from the bare side rises, due to the surface diffusion of the barium over the surface of the tungsten. Below 900° K. this surface diffusion rate is too slow to be measured, whilst above 1150° K. evaporation of the barium from the surface becomes a serious factor.

Following the appearance of L. de Broglie's papers on wave mechanics Elsasser (*Naturwiss.* p. 711, 1925) predicted that experimental evidence of the wave character of electron beams would be found in their reaction with single crystals. The experiments of G. P. Thomson (*Proc. Roy. Soc.* A, CXVII. 600, 1928; CXIX. 651, 1928) on the scattering of fast electrons 29,000–30,000 volts through thin metallic films, and of Davisson and Germer (*P.R.* XXX. 705, 1927; *P.N.A.S.* XIV. 619, 1928) and Rupp (*Ann. de Phys.* I. 773, 801, 1929; *Naturwiss.* LXXXV. 981, 1928) with slow electrons, 30–300 volts, diffracted by crystals and ruled gratings, have established experimentally the fundamental equation $\lambda = \frac{h}{mv}$, where λ is the wave length associated with a particle of mass m moving with velocity v.

Davisson and Germer (*loc. cit.*) and later Germer (*Zeit. f. Physik*, LIV. 408, 1929) have examined the beams scattered from a nickel crystal when bombarded with electrons of known velocity. As in the parallel case of X-rays the positions of maximum scattering will depend upon the lattice distance d, the wave length λ and the angle of scattering θ in such a way that the Bragg law

$$2d \sin \theta = n\lambda$$

is obeyed. By observing the effects of heating the crystal in a high vacuum *ca.* 10^{-8} mm. to drive off adsorbed gas they were able to distinguish four different kinds of scattered beams due respectively to scattering from (1) the space lattice of the nickel crystal, (2) the top layer of nickel atoms, (3) a monatomic gas layer, and (4) what was assumed to have been a thicker gas layer, but may in reality have been gas in solution in the metal. They concluded that the first layer of gas atoms which settled down after heating the crystal was arranged over the (111) plane in such a manner that each gas atom or molecule covered three nickel atoms and was separated from the plane by a distance of about 3 Å. In other words since nickel has a face centred cubic lattice the gas atoms above the (111) plane occupy positions immediately above nickel atoms in the third plane and thus shield the three nearest nickel atoms in the top layer, leaving only one nickel atom in four uncovered. Thus the spacing of gas atoms from one another is twice that for the underlying nickel atoms and the distance between the first gas layer and the top layer of nickel atoms is 50 % larger than the distance between adjacent planes of nickel atoms.

They further found on warming the crystal to less than 150° C. that the regular structure of the first gas layer disappeared although the gas was still on the surface and capable of weakening the beams scattered from the underlying nickel atoms. They attribute this to the melting or surface vaporisation of a two-dimensional solid film but give no critical temperature. They were not able to assign a definite structure to the gas in the deeper layers and no attempt was made to find out what the gas was.

These considerations of surface mobility have led Volmer (*loc. cit.*) to consider that an adsorbed gaseous phase on solid surfaces behaves as a two-dimensional gas and that two-dimensional gas laws are applicable (see p. 62).

The exact relationship between the two-dimensional gas pressure F and the three-dimensional gas pressure p above the surface naturally depends on the equation of state, for the two-dimensional system (see p. 67). Magnus (*Zeit. anorg. Chem.* CLV. 67, 1926; *Zeit. Elektrochem.* XXXIV. 1928) inclines to the view that, since the rate at which gas in the adsorbed film evaporates horizontally by leaving the edge of a plane surface of a crystal must be equal to the rate at which gas enters the film by a similar process, F must always be proportional to p. This conclusion is not necessarily justified, for under conditions of equilibrium the activities only of the gases in the two phases and not necessarily the pressures must be identical (this is especially the case for the gas in the surface phase).

We shall note that at least the experimental data obtained on the influence of temperature on the adsorption maximum give some support to the view that the limit for an adsorbed gas on a uniform solid surface is set by a characteristic limiting two-dimensional pressure F_t.

9. The adsorption potential.

An attempt to develop an adsorption isotherm, on the assumption of the mutual attraction by the gas molecules and by an attractive field outside the solid surface similar in character to the Van der Waals forces of molecular attraction, was first made by Williams (*Proc. Roy. Soc. Edin.* XXXVII. 161, 1917; XXXVIII. 23, 1918; XXXIX. 48, 1919; *Proc. Roy. Soc.* A, XCVI. 287, 298, 1919). Williams shows that the change in energy E which occurs on adsorption of one grm. mol on an infinite amount of adsorbent is

$$E = RT^2 \left(\frac{\partial \log c}{\partial T}\right) \quad \dots\dots\dots\dots\dots\dots\dots (1),$$

where c is the concentration of the gas in equilibrium with the interface. Later he derives two other expressions for this energy

$$E = RT \log \frac{x}{wc} \quad \dots\dots\dots\dots\dots\dots\dots (2),$$

where x is the amount of gas adsorbed, $w = A\,(\delta - \sigma)$, A is the area, δ the thickness of the adsorption layer and σ the diameter of the molecule of the adsorbed gas. He assumes the existence of an attractive force of a Van der Waals character

$$E = \int_{\infty}^{r_0} \mu a^{\frac{1}{2}}\, a_0^{\frac{1}{2}}\, \phi' r\, dr,$$

where μ is a universal constant, $a_0^{\frac{1}{2}}$, $a^{\frac{1}{2}}$ the Van der Waals' adhesions for adsorbent and adsorbate respectively and r the distance of the molecule from the surface, thus

$$E = \mu a^{\frac{1}{2}}\, a_0^{\frac{1}{2}}\, \phi\,(r_0) \quad \dots\dots\dots\dots\dots\dots\dots (3).$$

From (1) and (2) we obtain

$$\frac{dT\log\frac{x}{c}}{dT}=\log w \text{ or } T\log\frac{x}{c}=\text{constant}+T\log w-\int_0^T\frac{T}{w}\left(\frac{dw}{dT}\right)dT,$$

where the constant is a function of x but independent of T.

From (2) and (3) we obtain

$$T\log\frac{x}{c}=T\log w+\frac{\mu a^{\frac{1}{2}}\,a_0^{\frac{1}{2}}\,\phi r_0}{R}.$$

If we assume that w is independent of T, then as

$$\frac{\mu a^{\frac{1}{2}}\,a_0^{\frac{1}{2}}\,\phi r_0}{R}$$

is also independent of T, we obtain

$$T\log\frac{x}{c}=A+BT,$$

or $$\log\frac{x}{c}=\frac{A}{T}+B \quad \text{.....................(4)},$$

which is the adsorption isostere of Williams, who applied it successfully to the data of Titoff, Homfray, Richardson and Chappuis.

If B and A are not independent of T we may expand in powers of x,

$$\log\frac{x}{c}=B'+\left(\frac{\partial B}{\partial x}\right)_{x=0}x+\frac{A'}{T}+\frac{1}{T}\left(\frac{\partial A}{\partial \alpha}\right)_{x=0}+\dots,$$

or approximately $$\log\frac{x}{c}=A_0-A_1x,$$

the adsorption isotherm of Williams.

It is interesting to note that if we take the Langmuir equation (see p. 194)

$$\frac{\theta'}{\tau}=\alpha\nu\theta=\alpha kp\,(1-\theta'),$$

or $$\frac{\theta'}{p}=\alpha k\tau\,(1-\theta'),$$

by taking logarithms we obtain the Williams equation

$$\log\frac{\theta'}{p}=\log\tau\alpha\kappa+\log(1-\theta')=\log\tau\alpha\kappa-\theta' \text{ approximately},$$

for small values of θ', or $\log\dfrac{x}{p}=A_0-A_1x$.

An equation of a similar form may likewise readily be obtained by a simple consideration that if the potentials of the bulk and gaseous phases in equilibrium are equal, the free energy of the gaseous phase is $RT \log p$. If there is a difference of free energy between bulk and surface phase of λ then that of the surface phase is

$$RT \log p + \lambda \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(5).$$

Adopting the equation $F(A - B) = iRT$ to represent the behaviour of the surface phase, its free energy is

$$\int F dA \quad \text{or} \quad iRT \log \frac{iRT}{A - B} + \frac{BiRT}{A - B} \quad \ldots\ldots\ldots(6).$$

Replacing the surface area per grm. mol A by the surface concentration $x = \frac{1}{A}$, on equating (5) and (6) we obtain

$$iRT \log \frac{iRTx}{1 - Bx} + \frac{BiRTx}{1 - Bx} = RT \log p + \lambda \quad \ldots(7).$$

On neglecting the product Bx we obtain

$$i \log (iRT) \frac{x}{p^{\frac{1}{i}}} = \frac{\lambda}{RT} - (Bi)\, x.$$

If no lateral adhesion exists then $i = 1$ and we obtain

$$\log RT \frac{x}{p} = \frac{\lambda}{RT} - Bx \quad \ldots\ldots\ldots\ldots\ldots\ldots(8).$$

Williams has attempted in the case of the adsorption of sulphur dioxide to calculate δ, the thickness of the adsorption layer, and finds it of the order of one molecular thickness.

Eucken (*Verh. d. D. Phys. Ges.* XVI. 349, 1914; *Zeit. Elektrochem.* XXVIII. 6, 257, 1922) and Polanyi (*Verh. d. D. Phys. Ges.* XVIII. 55, 1916; *Zeit. Elektrochem.* XXVI. 370, 1920; *Festschrift Kaiser Wilhelm Ges.* p. 171, 1921; *Zeit. physikal. Chem.* CXXXII. 371, 1928) have likewise introduced the concept of an adsorption potential to obtain an adsorption isotherm.

Eucken in agreement with Williams assumes an adsorptive force similar to that of the Van der Waals' "a" constant and independent of the temperature, but also a repulsive force, so that the potential at any point distant x from the surface is given by

$$\phi = -\frac{K}{\delta^n} + \frac{K'}{\delta^m} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(9).$$

At the position of equilibrium $\left(\frac{d\phi}{d\delta}\right)_{\delta=\delta_0} = 0$,

hence $$\phi = -K\left(\frac{1}{\delta^n} - \frac{n}{m\delta_0^{n-m}}\frac{1}{\delta^m}\right) \quad \text{.........(10)}.$$

Since the potential varies with the distance from the surface the concentration in various layers parallel with the surface will likewise vary; this concentration in any one layer is assumed to be determined by the Boltzmann equation

or $$x_\delta = x_\infty \, e^{-\frac{\phi}{kT}} \quad \text{........................(11)},$$

where ϕ is the potential at a distance δ from the surface.

The total adsorption per sq. cm. is accordingly

$$\int_{\delta_0}^{\infty} (x_\delta - x_\infty)\, dx = x_\infty \int_{\delta_0}^{\infty} (e^{-\frac{\phi}{kT}} - 1)\, dx.$$

Inserting the value of ϕ from (9) in this equation Eucken obtains

$$x = \frac{x_\infty \, \delta_0}{\frac{nC}{T} - b\,(n, m)} e^{\frac{C}{T}}, \quad \text{where } C = \frac{K}{\delta_0{}^n k}\left(1 - \frac{n}{m}\right) \text{...(12)},$$

and b a function of n or m is usually small. Since $x_\infty = \frac{p}{kT}$ and $b\,(n, m)$ is negligibly small compared with $\frac{nC}{T}$ we obtain

$$x = \frac{p}{kn}\frac{\delta_0 e^{\frac{C}{T}}}{C},$$

or $$\log x = \log p + \frac{C}{T} + i \quad \text{..............(13)},$$

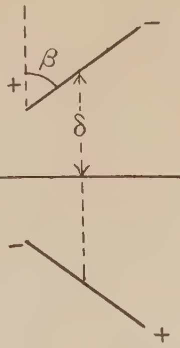
an equation of the same form as that of Williams.

Polanyi likewise assumes a force field extending from the surface and regards a surface as presenting a definite field thickness or a finite absorption volume. We shall have occasion to refer to this view in a subsequent section.

10. Electrical forces in adsorption.

(a) *On dielectrics.*

Several attempts have been made to obtain an adsorption isotherm in terms of electric forces. For the evaluation of these forces certain assumptions are made as to the nature of the adsorbing surface. Lorenz and Landé (*Zeit. anorg. Chem.* CXXIV. 47, 1922), Jaquet (*Theorie der Adsorption von Gasen*, Berlin, 1925) and Blüh and Stark (*Zeit. f. Physik*, XLIII. 575, 1927) have shown that if the gas undergoing adsorption possesses an electric moment and is further capable of undergoing polarisation or deformation, adsorption onto a dielectric surface will occur owing to the attraction exerted by the electrical mirror image formed in the body of the adsorbing surface. We may consider the simple case of an unpolarisable molecule of permanent electric moment $\mu = el$.



The potential energy of the dipole at a distance δ above a surface in which its mirror image is situated is

$$\phi = -\frac{e^2 l^2}{8\delta^3}(1 + \cos^2\beta).$$

The molecule can break away from the surface when its kinetic energy exceeds that of the induced electrical attraction. Assuming the usual statistical distribution, the number of molecules held at a distance δ from the surface and making an angle between β and $\beta + \delta\beta$ with the normal will be

$$x_\delta(\beta)\,(2\pi\,.\,d\cos\beta) = x_\infty\, e^{\frac{e^2l^2}{8\delta^3kT}(1+\cos^2\beta)}\, d\,2\pi\,.\,d\cos\beta.$$

Hence $$x_\delta = \int \frac{x_\delta(\beta)\, 2\pi d\cos\beta}{4\pi} = x_\infty\, e^y \int_0^1 e^{yz^2}\, dz,$$

where $z = \cos \beta$ and $y = \frac{e^2 l^2}{8\delta^3 kT}$. Putting further $\sqrt{y}z = m$ we obtain

$$x_\delta = x_\infty \frac{e^y}{\sqrt{y}} \int_0^{\sqrt{y}} e^{m^2} dm,$$

which on integration with $y \gg 1$ becomes

$$x_\delta = x_\infty \frac{e^{2y}}{2y}.$$

If the distance of nearest approach of a dipole to the surface be δ_0 the total amount adsorbed per sq. cm. will be

$$x = \int_{r_0^3}^{\infty} (x_\delta - x_\infty)\, d\delta = \frac{x_\infty}{12} \sqrt[3]{\frac{e^2 l^2}{kT}} \int_0^{y_0} \left(\frac{e^{2y}}{y} - 1\right) \frac{dy}{y^{1+\frac{1}{3}}},$$

where $$y_0 = \frac{e^2 l^2}{8\delta_0{}^3 kT} = \frac{\mu^2}{8\delta_0{}^3 kT} = \frac{C}{2T},$$

whence $$x = \frac{x_\infty \delta_0}{3} \frac{e^{2y_0}}{(2y_0)^2},$$

which, on inserting $$x_\infty = \frac{p}{kT},$$

is equal to $$\frac{p\delta_0 T}{3kC^2} e^{\frac{C}{T}},$$

an equation to be compared with $x = \frac{p\delta_0}{knC} e^{\frac{C}{T}}$ for the isotherms of Williams and Eucken.

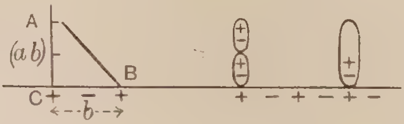
For the adsorption of a gas consisting of molecular quadripoles the corresponding equation is

$$x = \frac{p \,.\, \delta_0}{10\sqrt{6}\; 2{\cdot}6\; Ck} \frac{e^{\frac{2\cdot 6\, C}{T}}}{2{\cdot}6 \frac{C}{T}}.$$

We may observe that taking as magnitude of the electric moment $\mu = 1 \,.\, 10^{-18}$ E.S.U. at 300° K. the value of $y_0 = \frac{\mu^2}{8\delta^3 kT}$ decreases rapidly with an increase in the value of δ. Inserting the values for $2\delta = 2$, 3 and 4 Å. respectively y_0 becomes 4·8, 1 and 0·4 respectively. Since molecular magnitudes preclude a distance much less than 2 Å. for δ, or 4 Å. for 2δ, it is clear that the hypothesis of adhesion by mirror image forces alone is scarcely adequate.

(*b*) *On heteropolar surfaces.*

If an adsorbing heteropolar crystal surface be regarded as consisting of alternate positive and negative charges such as is exhibited by the 100 plane of a rock-salt crystal, the electrostatic attraction and repulsion due to these charges can be evaluated. Simple derivations for the form of the adsorption isotherm on such a surface have been made by Blüh and Stark (*Zeit. f. Physik*, XLIII. 575, 1927), by Boer (*Ver. Kon. Akad. Wet. Amst.* XXXVII. 237, 1928), and by Boer and Zwikker (*Zeit. physikal. Chem.* CXXXIII. 407, 1929), whilst a more exhaustive investigation of all the forces operative at such surfaces has been carried out by Lennard Jones and Dent (*Trans. Farad. Soc.* XXIV. 93, 1928). We may note that the adsorption of dipoles onto a surface by the ionic charges to form multimolecular layers is determined not only by the magnitude of the dipole μ and its deformability α, the energy necessary to form a dipole on the surface being $\frac{\mu^2}{2\alpha}$ where μ is the induced dipole moment, but also by the position of the dipole in the molecule.



The potential energy between two dipoles each of moment μ separated by a distance δ is $\frac{\mu^2}{\delta^3}$. Inserting the reasonable values of $\mu = 2 . 10^{-18}$ E.S.U. and $\delta = 5$ Å. for the molecular diameter we obtain a potential energy of the order of only 1000 cals. per grm. molecule. For molecules containing a non-polar group with the electric moment residing chiefly in the polar head (see Ch. VII) the adhesional forces of the second layer due to their mutual attraction will evidently decrease rapidly with chain length and the adhesional potential energy will soon become comparable with the kinetic energy of thermal agitation, *ca.* 600 cals. per grm. molecule, thus precluding the building up of such layers. Confining our attention to the electrostatic attraction of the charges in the surface for the adsorbed dipole in the first layer as has been done by Boer and Zwikker, if ab be the distance of the dipole of moment μ from the lattice, of lattice constant b, the attraction of the dipole for the surface will be for the first two charges

$$\phi = \frac{2e\mu}{a^2b^2} + \frac{2e\mu}{AB^2} \cos BAC = \frac{2e\mu}{b^2}\left(\frac{a}{a^2 + 2^2}\right)^{\frac{3}{2}} .$$

On summation over the surface we obtain

$$\phi = \Sigma \frac{2ae\mu}{b^2} [a^2 + 2n^2 + 2m^2]^{-\frac{3}{2}}$$

$$= S \frac{e\mu}{b^2} ,$$

where n and m are integers of all values.

Since the energy of the dipole is $\frac{\mu^2}{2\alpha}$, we obtain if there be but one layer

$$\phi = \frac{\mu^2}{2\alpha} - S \frac{e\mu}{b^2} .$$

Under conditions of equilibrium $\frac{d\phi}{d\mu} = 0$, whence $\mu = \frac{\alpha Se}{b^2}$ and

$$\phi = - \frac{S^2 e^2 \alpha}{2b^4} .$$

We can calculate the values for the case of iodine adsorbed onto calcium fluoride with α for iodine as *ca.* 5 . 10^{-24}, $b = 1{\cdot}93$ Å. for the CaF_2 lattice. S is found to be 0·36, whence

$$\phi = - \frac{(0{\cdot}36)^2\,(4{\cdot}77)^2\,5}{2 \times (1{\cdot}93)^4} . 10^{-12} \text{ ergs},$$

which is equivalent to a heat of adsorption of 7,600 cals. per grm. atom. The electric moment of the adsorbed iodine is found to be no less than $\mu = 2{\cdot}3 . 10^{-18}$ E.S.U., a large value, indicating that the distortion produced on adsorption is extremely great. We may remark that Boer (*loc. cit.*) noted that the limit of the absorption spectrum was 2950 Å. for the adsorbed iodine, a value to be compared with 3500 Å. in aqueous KI, 4300 Å. in alcohol, and 5100 Å. in chloroform, the surface phase thus appearing comparable to a highly polar solvent.

For multimolecular layers Boer and Zwikker have in a similar manner calculated the potential energies and electric moments of the adsorbed molecules in each layer, obtaining the general expressions

$$\mu_{n-1} = \frac{\mu_n}{K} = \frac{A}{\beta}\left(\frac{K}{1-K^2}\right)^{n-1},$$

$$\phi_n = \frac{\beta}{2}\mu_n{}^2 + \gamma\mu_{n-1} = -\frac{A^2}{2\beta}\left(\frac{K}{1-K^2}\right)^{2n-2},$$

where A, β and K are constants involving the lattice constants and deformability.

The general equation for the vapour pressure is

$$\log p = -\frac{(\lambda_a{}' - \phi_n)}{RT} + i,$$

where $\lambda_a{}'$ is the latent heat of evaporation in the adsorbed state at absolute zero and $\lambda_a{}' - \phi_n$ is the isothermal heat of adsorption, i the integration constant of the vapour-pressure equation.

Over the liquid surface we have $\log p_0 = -\dfrac{\lambda_0{}'}{RT} + i_0$.

Hence $$\log\frac{p}{p_0} = \frac{\phi_n}{RT} + \frac{\lambda_0{}' - \lambda_a{}' + RT\,(i - i_0)}{RT}.$$

If we put $$e^{\frac{\lambda_0{}' - \lambda_a{}' + RT\,(i - i_0)}{RT}} = K_3,$$

we obtain $$\log\frac{p}{p_0 K_3} = \frac{\phi_n}{RT} = \frac{A^2}{2\beta RT}\left(\frac{K}{1-K^2}\right)^{2n-2}.$$

If we put $\left(\dfrac{K}{1-K^2}\right)^2 = K_1$ and $\dfrac{A^2}{2\beta RTK_1} = K_2$ we obtain as an adsorption isotherm

$$\log\frac{p}{p_0 K_3} = K_2 K_1{}^n.$$

Boer finds for the adsorption of iodine on calcium fluoride that n is unity, but for the adsorption on barium chloride a knowledge of three constants is necessary.

A much more detailed investigation has been carried out by Lennard Jones and Dent (*Trans. Farad. Soc.* XXIV. 93, 1928) in which it is shown that three separate effects have to be considered in evaluating the adsorption of a gas on such a heteropolar surface. Firstly the electrostatic field outside the plane doubly periodic charged surface is determined in some detail following the method of Born (*Atomtheorie des festen Zustandes*, 2nd ed. 1923) by calculating the separate effects of each layer of ions. In the following table are given the magnitude of these forces for the 100 plane of a uniunivalent crystal, e.g. NaCl, in which the distance between 2 ions is given by $b = 2{\cdot}815$ Å. For other crystals the forces outside the respective 100 planes can be calculated by multiplying by $\frac{\eta_2 b_1^2}{b_2^2}$, where η_2 is the valency of the charges in the second crystal and $\frac{b_1}{b_2}$ the ratio of the sides of the unit cells.

Distance from plane = δ, $2b = 5{\cdot}63$ Å.

$\frac{\delta}{2b}$	$\frac{1}{2}$	$\frac{7}{12}$	$\frac{8}{12}$	$\frac{9}{12}$	$\frac{10}{12}$	$\frac{11}{12}$	1
$e\phi\delta \times 10^{13}$ ergs	5·36	2·45	1·23	0·64	0·28	0·14	0·06

The work to separate a permanent dipole of length l is

$$e\,[\phi\delta - \phi\,(\delta + l)].$$

With a dipole of permanent strength $5 \,.\, 10^{-18}$ E.S.U. at a distance of 2·5 Å. we obtain a value of $3 \,.\, 10^{-13}$ ergs for the work of separation, equivalent to 4,500 cals. per grm. molecule. The second factor which is considered is the polarisation of a neutral molecule in the electrostatic field of the crystal, the factor considered by Boer and Zwikker. We may cite some values for the magnitude due to this cause for a molecule of polarisability $\alpha = 1{\cdot}63 \,.\, 10^{-24}$ near the surface of the crystal with the same lattice constants given above:

$\frac{\delta}{2b}$	0·5	0·6	0·7	0·8	0·9	1·0	1·5
$\phi^p\delta$ ergs	$2{\cdot}56 \times 10^{-14}$	$4{\cdot}27 \times 10^{-15}$	$7{\cdot}20 \times 10^{-16}$	$1{\cdot}22 \times 10^{-16}$	$2{\cdot}06 \times 10^{-17}$	$3{\cdot}48 \times 10^{-18}$	$4{\cdot}80 \times 10^{-22}$

It will be noted that the potential falls off rapidly as the distance is increased and is much less than the force due to the electrostatic attraction, the values of which are given above.

The value of $\phi^p\delta$ is proportional to the polarisability α and to the inverse fifth power of the lattice constant b.

Of greater importance are shown to be the Van der Waals cohesive forces in which the repulsive and attractive fields between molecules are assumed to be in the form of

$$\frac{\lambda}{\delta^n} - \frac{\mu}{\delta^m}.$$

For most gases $m = 5$ is regarded as most satisfactory. For the solid surface of the uniunivalent crystal the ions are assumed to possess argon-like ores. Dent and Lennard Jones have evaluated the Van der Waals attractive force for a surface of such a structure and obtain the following values for the force in dynes and the potential energy in ergs with the value of

$$\mu = \frac{\rho}{b^3} = 1{\cdot}63 . 10^{-43} \text{ and } m = 5.$$

$\frac{\delta}{2b}$	0·5	0·7	1·0	1·5
H dynes	$1{\cdot}92 \times 10^{-5}$	$7{\cdot}39 \times 10^{-6}$	$3{\cdot}02 \times 10^{-6}$	$1{\cdot}16 \times 10^{-6}$
$\phi^w\delta$ ergs	$4{\cdot}97 \times 10^{-13}$	$1{\cdot}92 \times 10^{-13}$	$7{\cdot}56 \times 10^{-13}$	$2{\cdot}78 \times 10^{-14}$

We note that the Van der Waals forces are long distance forces in contrast to the electrical forces.

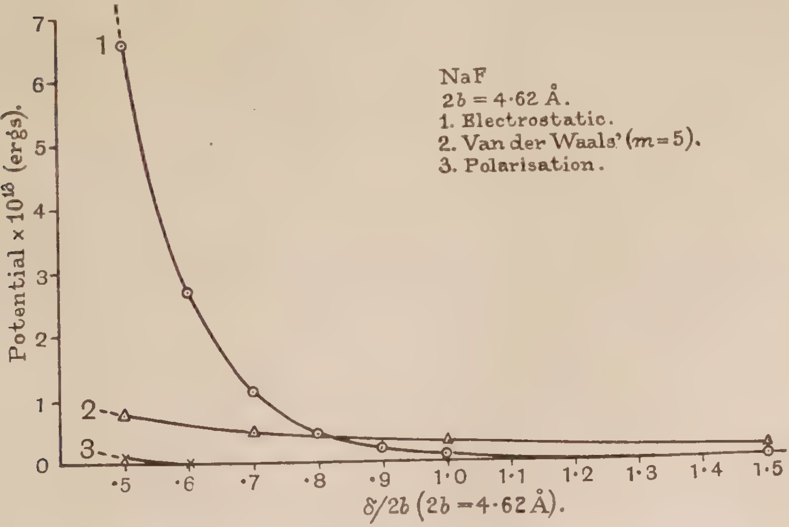
Finally the authors consider the polarisation of the crystal due to the charge outside it, similar to the mirror image forces considered by Lorenz and Landé, and this is found to be relatively small.

The data on p. 213 taken from the paper of Lennard Jones and Dent give the contribution of the electrostatic, the Van der Waals and the polarisation potentials on a charged particle and neutral atom respectively.

A simple application of these figures has been made to calculate the heat of adsorption of argon on KCl. Using the usual repulsive force constants a rough calculation shows the equilibrium distance to be about $1{\cdot}2b$. The corresponding value of ϕ is $1{\cdot}6 . 10^{-13}$ ergs, so that the heat of adsorption of one gram molecule (neglecting the influence of the molecules on each other) is about 2000–1500 calories.

The results can be further applied to estimate the concentration of atoms in the neighbourhood of a solid by Boltzmann's formula ($n = n_0 e^{\phi/kT}$). Assuming an inverse fifth power attraction, the indication is that the concentration of argon at a distance of 10 Å. from KCl is about two to three times the normal at room temperature.

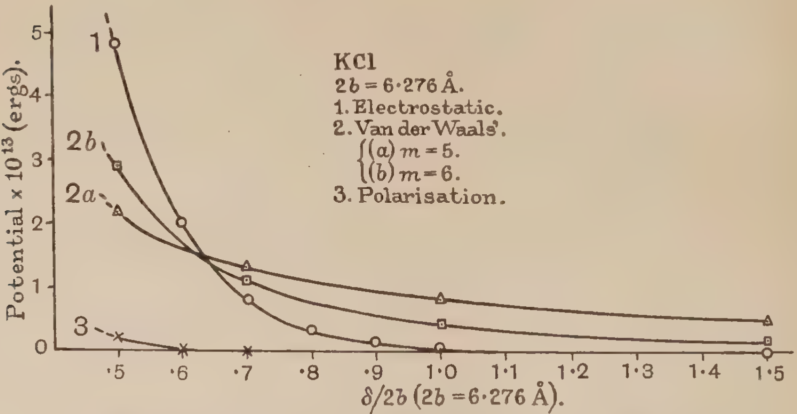
	$\frac{\delta}{2b}$	0·5	0·7	1·0	1·5
Neon and NaF	Electrostatic	$1{\cdot}26 \times 10^{-4}$	$2{\cdot}11 \times 10^{-5}$	$1{\cdot}47 \times 10^{-6}$	$1{\cdot}72 \times 10^{-8}$
	Polarisation	$5{\cdot}29 \times 10^{-6}$	$1{\cdot}48 \times 10^{-7}$	$7{\cdot}11 \times 10^{-10}$	$9{\cdot}89 \times 10^{-14}$
	V. d. Waals ($m = 5$)	$5{\cdot}46 \times 10^{-6}$	$2{\cdot}11 \times 10^{-6}$	$8{\cdot}60 \times 10^{-7}$	$3{\cdot}31 \times 10^{-7}$
Argon and KCl	Electrostatic	$6{\cdot}80 \times 10^{-5}$	$1{\cdot}14 \times 10^{-5}$	$7{\cdot}94 \times 10^{-7}$	$9{\cdot}30 \times 10^{-9}$
	Polarisation	$4{\cdot}74 \times 10^{-6}$	$1{\cdot}33 \times 10^{-7}$	$6{\cdot}36 \times 10^{-10}$	$8{\cdot}85 \times 10^{-14}$
	V. d. Waals ($m = 5$)	$1{\cdot}11 \times 10^{-5}$	$4{\cdot}28 \times 10^{-6}$	$1{\cdot}75 \times 10^{-6}$	$6{\cdot}70 \times 10^{-7}$
	($m = 6$)	$2{\cdot}84 \times 10^{-5}$	$7{\cdot}00 \times 10^{-6}$	$1{\cdot}88 \times 10^{-6}$	$4{\cdot}58 \times 10^{-7}$



The Potential Field outside a (100) plane of NaF on (1) a charged particle, (2) on Neon.

(*c*) *Adsorption on metallic surfaces.*

In the previous sections we have considered briefly the development of the electrical theory of adsorption by mirror image forces on dielectrics and by the mirror image forces as well as the forces due to electric charges on ionic lattices. It is clear that the phenomenon of adsorption on the surfaces of conductors such as metals or charcoal cannot be resolved by the methods outlined above unless some definite concept is made as to the nature of the electrical forces at the surface. Information in this field has been provided chiefly from the study of thermionic emission.



The Potential Field outside a (100) plane of KCl on (1) a charged particle, (2) on Argon.

The work done by an electron escaping from a metal surface may be regarded as made up of two parts, the work due to the image forces from a long distance away down to a limiting distance δ_0 and the work done in moving from δ_0 into the metal, through the intrinsic field, which work is assumed to be constant (Schottky, *Phys. Zeit.* xv. 872, 1914). Since the work functions of metals vary from some 1 to 8 volts the intrinsic field thickness δ_0 extends from 16 to 1 Å. in thickness. Although the characteristics of the intrinsic field are not known in detail it is certain that beyond small distances only image forces are operative.

The thermionic properties of a body depend very largely upon the state of its surface and afford a convenient means of investigating surface films on solid metals. The qualitative effects of such films have been known for many years but the development of quantitative measurements is comparatively recent and is due in the first place to I. Langmuir and his collaborators.

In order that an electron may escape from a body it must do a certain amount of work in passing through its surface. A foreign atom on the surface is electrically equivalent to a dipole and gives rise to an added electric field at the surface. This electric field may either assist or impede the escape of electrons according to its direction. Thus electro-negative atoms like oxygen lower the electron emission and electro-positive atoms like sodium increase it.

The thermionic emission from a clean surface is given by Richardson's equation

$$i = AT^2 \epsilon^{-\frac{\phi}{kT}} \quad \text{.........................(1)},$$

where i is the current per sq. cm., T is the absolute temperature of the emitting surface, and A and ϕ are constants for any given element. The exact theoretical significance of this equation is still a matter of dispute (cf. Fowler, *Proc. Roy. Soc.* A, CXXII. 36, 1929) but it is sufficient for the present purpose that it represents the experimental results satisfactorily and that the constant ϕ is a measure of the work done by an electron in escaping from the metal, on any theory. It will be appreciated that a small change in ϕ will have an enormous effect on the emission; it is actually found that a monatomic layer of thorium on a tungsten surface at 1500° gives an electron emission one hundred thousand times greater than that from a clean tungsten surface. Thus thermionic measurements are a very sensitive method of following surface changes.

The change in potential V produced by a surface layer is given by Helmholtz's equation (see p. 30)

$$V = 4\pi M \times 300 \quad \text{.....................(2)},$$

where M is the electric moment per sq. cm. and may be written

$M = Np$, where N is the number of atoms per sq. cm. and p is the electric moment of each atom. The decrease or increase in the work that an electron must do is therefore proportional to the concentration of atoms in the surface layer, or in other words to the fraction θ of the surface covered. Richardson's equation (1) for a surface partly covered by a film thus becomes

$$i_\theta = AT^2 \epsilon^{\frac{\phi + \alpha\theta}{kT}} \quad \text{......................(3).}$$

The sign of α will depend upon the nature of the adsorbed atoms.

If the temperature is constant

$$\Delta \log i_\theta \propto \Delta\theta \quad \text{......................(4).}$$

Let i_0 be the emission from the clean surface, then equation (4) becomes

$$k (\log i_\theta - \log i_0) = \theta \quad \text{................(5).}$$

If i_1 is the emission from a fully covered surface ($\theta = 1$) then

$$k (\log i_1 - \log i_0) = 1 \quad \text{................(6).}$$

Eliminating k from equations (5) and (6) we get

$$\theta = \frac{\log i_\theta - \log i_0}{\log i_1 - \log i_0} \quad \text{...................(7).}$$

Equation (7) enables us to deduce the fraction of the surface covered at any given temperature from measurements of the thermionic emission and is thus of great importance. In its derivation the assumption has been made that the effects of the separate atoms are additive. It is however probable that this may not be true for concentrated films, due to interaction between the close packed atoms (see p. 338); and it is actually found for instance that while dilute caesium films on tungsten increase the emission concentrated films produce a reversal of this effect. Thus equation (7) is only applicable to dilute films*.

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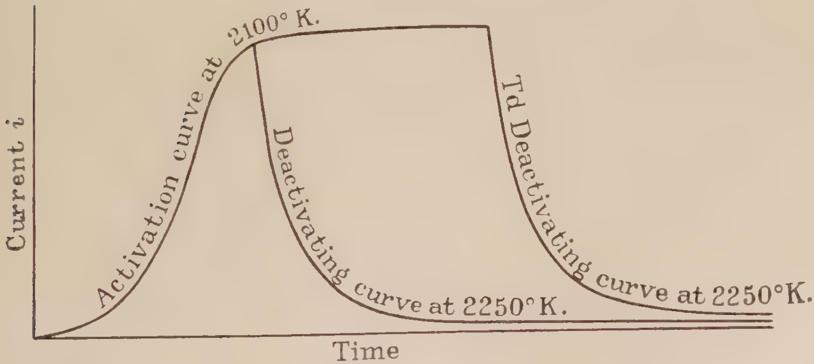
* It has been verified experimentally for dilute caesium films. J. A. Becker (*Phys. Rev.* xxxiii. 1082 (Abstract), 1929) has found the following empirical relation to be more accurate for barium

$$\log i_\theta / \log i_0 = 1{\cdot}1 \, (\log i_1/i_0) \, (1 - \epsilon^{-20});$$

the electric moment contributed by a barium atom in a film appears to be about twice as great when the surface is only covered to the extent of 10 % as when a loose packed film is present.

We have only considered the action of the surface layer in changing the value of the constant ϕ in Richardson's equation; in practice the value of A is also changed but the effect is small compared with that due to the change in ϕ.

The effect of thorium in increasing the emission from a tungsten filament was discovered by I. Langmuir (*Phys. Rev.* IV. 544, 1914). Thoria was originally added to tungsten to prevent "offsetting" (flow between crystals) of lamp filaments. By heating the filament to 2900° for a minute the thoria is reduced to thorium which diffuses up to the surface and then evaporates off. The rate at which the thorium film grows is simply the difference between the rates of diffusion and evaporation. The growth of the thorium film at any time is best observed by momentarily lowering the filament temperature to some standard testing temperature (say 1500°) at which the rates of evaporation and diffusion are negligible; this enables the measurements to be carried out without undue haste (Langmuir, *Phys. Rev.* XXII. 357, 1923).



In the figure is shown a typical curve obtained with a forming or activating temperature of 2100° and a testing temperature of 1500°. A deactivation curve is also shown corresponding to a temperature T_d; at this temperature the rate of evaporation E is greater than the rate of diffusion D. From such curves and the use of equation (7) together with the number of thorium atoms on the surface at maximum activation (this is discussed below) Langmuir deduced the following expressions for D and E:

$$\log_{10} D = 0{\cdot}21 - 20{,}900/T \quad \text{.............(8)},$$

$$\log_{10} E = 7{\cdot}76 - 44{,}500/T \quad \text{.............(9)}.$$

Knowing the rate of evaporation as a function of the temperature it is possible by the use of the Clapeyron-Clausius equation to deduce the heat of evaporation of thorium from a tungsten surface. Langmuir found that this heat of evaporation was 204,000 cals. per grm. atom. Mrs M. R. Andrews (*Phys. Rev.* XXXIII. 454, 1929) has redetermined the heat of evaporation by a series of measurements in which the thorium was deposited externally on the surface from an adjacent thoriated wire or by evaporation from a rod of thorium metal. The experimental conditions were thus greatly simplified. She found that the heat of evaporation of thorium from clean tungsten was 177,000 cals. per grm. atom; from carbonised tungsten it was 202,000 cals. per grm. atom.

Activation curves show that for dilute films the rate of growth of the thorium layer decreases as the layer is formed according to the expression

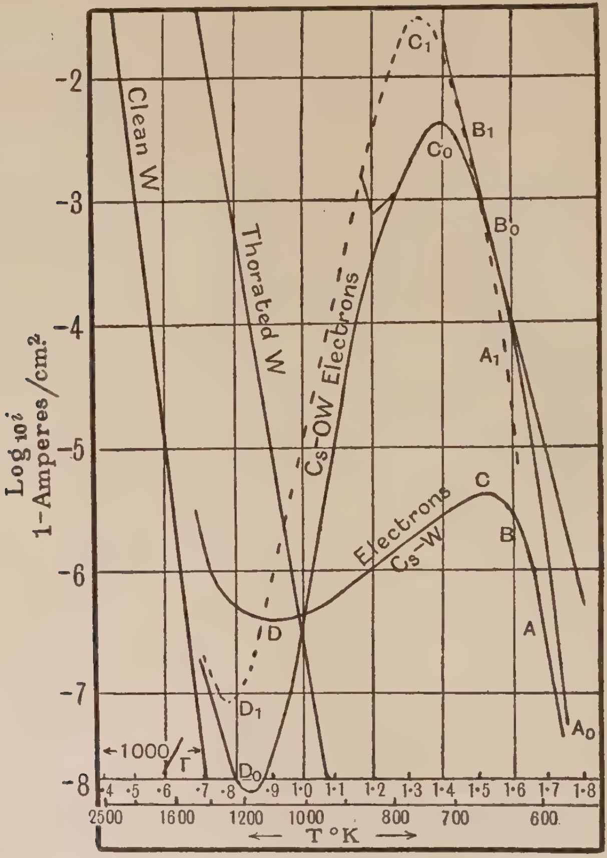
$$d\theta/dt = K\,(1 - \theta) \quad \text{.................(10)}.$$

This can be interpreted as meaning that the probability of a thorium atom finding a place on the surface is $(1 - \theta)$. If, as Langmuir supposed, the thorium atoms diffused up through the crystal lattice then such an interpretation is a plausible one. P. Clausing (*Physica*, VII. 193, 1927) has shown however that the diffusion of thorium atoms takes place only between crystal boundaries (a fact which is in accordance with the property of thoria of preventing offsetting). The atoms can therefore only reach the surface in certain places; under such conditions the probability of finding an empty spot will no longer be $(1 - \theta)$. It is perhaps relevant in this connection that Langmuir found that when θ is large the above expression breaks down and the factor $(1 - \theta)$ must be replaced by $(1 - {\cdot}82\theta - {\cdot}18\theta^3)$. If the thorium atom is unable to find a vacant place on reaching the surface it will evaporate; Langmuir has called this process "Induced Evaporation" to distinguish it from the normal spontaneous evaporation due to the thermal agitation of atoms on the surface. The induced evaporation increases as the surface becomes covered.

In a completed monatomic layer the atoms must be regularly spaced. Taking into account the roughness of a tungsten filament that has been subjected to heat treatment there are $1{\cdot}51 . 10^{15}$ tungsten atoms per sq. cm. (Langmuir, *Phys. Rev.* XXII. 357, 1923). The number of thorium atoms that can be packed into a plane lattice is $0{\cdot}91 . 10^{15}$ atoms per sq. cm. so that it is impossible for each tungsten atom to adsorb one thorium atom. It is reasonable to suppose that there are half as many thorium atoms as underlying tungsten atoms per sq. cm. since a fractional ratio is extremely improbable. Thus there are probably $0{\cdot}756 . 10^{15}$ thorium atoms per sq. cm. By the use of Richardson's equation the work done by an electron in escaping from a fully activated surface was found to be equal to the work done by an electron in moving against a potential difference of 2·62 volts (S. Dushman and J. W. Ewald, *Phys. Rev.* XXIX. 87, 1927). K. H. Kingdon (*Phys. Rev.* XXIV B. 510, 1924) obtained the value 2·68 volts. These values of the work of exit are smaller than that of pure thorium which C. Zwikker (*Proc. Acad. Amsterdam*, XXIV. 1, 1926) has found to be 3·39 volts. S. Dushman, D. Dennison and N. B. Reynolds (*Phys. Rev.* XXIX. 903, 1927) have shown that tungsten containing Yt, La, Ce, Zr or U behaves very like that containing thorium.

The adsorption of caesium on tungsten.

The adsorption of caesium on tungsten was first investigated by I. Langmuir and K. H. Kingdon (*Science*, LVII. 58, 1923). The problem is in some ways simpler than that of the adsorption of thorium since the caesium is deposited externally on the surface and the rate of deposition can be deduced from gas kinetic considerations. The figure (Becker, *Phys. Rev.* XXVIII. 341, 1926) shows the variation of the emission with the temperature of the filament, the rate of arrival of the caesium atoms being constant. As the temperature is increased (starting from the right-hand side of the abscissa) the emission rises in accordance with Richardson's equation for a fully covered tungsten surface. The emission reaches a maximum at C, falls to a minimum at D, and then rises again in approximate agreement with that from a clean tungsten filament *in vacuo*. The explanation of this curve is simple. At low temperatures the filament is completely covered with caesium; at a certain temperature the caesium begins to evaporate and the emission decreases with increasing temperature until the surface is practically free from



Log$_{10}$ i vs. 1000/T where i is the thermionic current per cm.^{2} and T is in °K. $ABCD$ represents electron emission from a tungsten filament in caesium vapour; $A_0B_0C_0D_0$ from an oxidised tungsten filament; $A_1B_1C_1D_1$ the same at a vapour pressure ten times as great.

caesium atoms. The emission then finally rises again as ordinary thermionic emission sets in. An interesting consequence of this characteristic is that if the filament heating current is switched off from a temperature above C, the emission is at first seen to rise as the filament cools down. One of the most interesting properties of a tungsten filament in caesium vapour is that the filament gives off a continuous supply of positive caesium ions. This is due to the fact that the ionisation voltage of caesium is lower than that of tungsten, so that if a caesium atom hits the filament its series electron will be torn off; at a sufficiently high temperature the positive ion is thrown off the surface; at lower temperatures the caesium sticks and an adsorbed layer is built up. The steady production of positive ions can only take place when the work of exit from the surface is above the ionisation potential of caesium. The adsorption of caesium lowers the work of exit, so that at low temperatures no positive ions are produced. Above a certain filament temperature further increase in the temperature causes no corresponding increase in the filament positive ion current—this can only mean that every atom hitting the filament is ionised. The positive ion characteristics have been determined by Becker. The total positive ion current is a direct measure of the number of atoms hitting the filament per second and thus the pressure of the caesium vapour in the bulb can be determined. This has been done by I. Langmuir and K. H. Kingdon (*Proc. Roy. Soc.* A, CVII. 61, 1925). If the work of exit of the tungsten filament is increased by oxidation it is possible to produce positive ions of any element whose ionisation potential lies below about 9 volts.

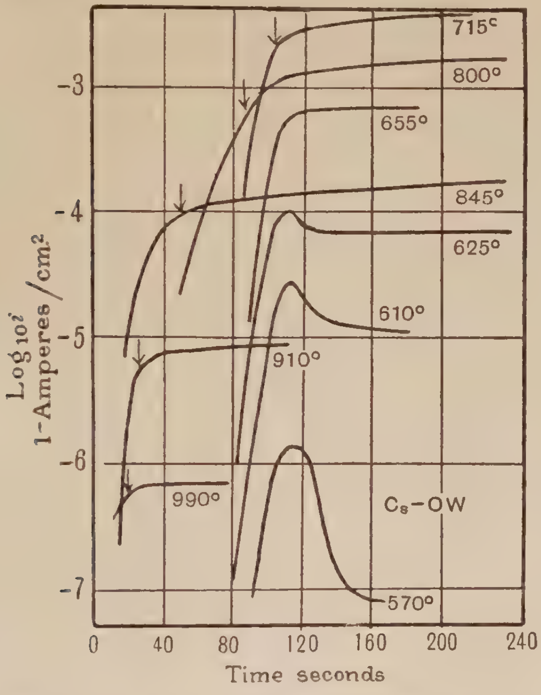
If the filament temperature is lowered a hysteresis effect is observed and the production of positive ions does not stop until the temperature is well below that at which ionisation began. This behaviour is strongly reminiscent of the hysteresis effects observed in the liquefaction of a gas or the solidification of a liquid, and Langmuir and Kingdon have suggested that in the hysteresis region the caesium can exist in two distinct phases. By using a number of collectors round the filament it is possible to show that one part of the filament may be emitting positive ions while another part may be covered with caesium, so that no ions are produced. The two regions are separated by a comparatively sharp dividing line which can be made to move backwards or forwards by altering the filament temperature.

By applying Saha's theory of thermal ionisation to the conditions at the surface of a tungsten filament in caesium vapour, Langmuir and Kingdon have been able to verify the Sackur-Tetrode value of the chemical constant.

The fact that above a certain temperature every impinging atom is ionised makes possible a very simple determination of the number of caesium atoms N_0 per sq. cm. at the optimum activity. It is only necessary, as J. A. Becker (*Phys. Rev.* XXVIII. 341, 1926) has shown, to measure the rate of arrival of the atoms and to find the time required to activate a clean filament. The positive ion current measures the rate of arrival of the atoms, and when this constant rate is multiplied by the time necessary for activation the number of atoms per sq. cm. is obtained. Becker's method of determining N_0 assumes that all the atoms striking the filament are able to stick to it. This was verified by observing that the product of the positive ion current and the time of formation always remains constant. Thus there is no induced evaporation as with thorium, so that the caesium atoms are probably in continual movement over the surface, as W. Schottky (*Handbuch d. exp. Physik*, VIII. pt 3, 192) has pointed out.

The figure opposite shows some activation curves obtained by Becker. It will be seen that at the lower filament temperatures the curves pass through a maximum. The peak corresponds to maximum activation and further deposition of caesium leads to a decrease in emission. Becker found N_0 to be $3{\cdot}7 . 10^{14}$ atoms per sq. cm. The number of caesium atoms in a hexagonally packed section of a body centred cubic lattice is $4 . 10^{14}$ atoms per sq. cm.; for a face centred lattice, which is another possible distribution, the number is $3{\cdot}8 . 10^{14}$ atoms per sq. cm. Thus there is some evidence that maximum activation is obtained with a completed monatomic film and the subsequent decrease in the emission must be due to the formation of a second layer; this is Becker's interpretation of his results. Langmuir and Kingdon (*Proc. Roy. Soc.* A, CVII. 61, 1925, and Kingdon, *Phys. Rev.* XXIV. 510,

1924) however consider that maximum activation is reached when $\theta = 0{\cdot}9$. Since we do not know accurately the number of caesium atoms in a monatomic film the question cannot be settled decisively.



The Cs—OW filament is heated to 1040° K. and positive ions are drawn. This removes practically all the adsorbed caesium. At time 0 the temperature is suddenly changed to the value indicated on each curve, the plate potential is reversed, and the $\log_{10}$ of the electron emission observed as time progresses. The time to reach the maximum at the three lower temperatures is called t_m.

Becker, from the measurements of Langmuir and Kingdon, found that the work of exit for a fully activated filament was 1·36 volts. For caesium on an oxidised tungsten filament Kingdon found a value of 0·71 volts.

Adsorption of atoms similar to caesium.

T. J. Killian (*Phys. Rev.* XXVII. 578, 1926) has investigated the adsorption of rubidium and potassium on tungsten and oxidised tungsten. These metals show effects similar to those of caesium but due to their lower vapour pressures higher bulb temperatures are necessary.

Adsorption of caesium and activated nitrogen on tungsten.

N. A. de Bruyne (*Camb. Phil. Soc.* xxv. 347, 1929) has shown that the addition of nitrogen to caesium vapour produces no new effects in the emission from a tungsten filament unless the nitrogen is activated by electron bombardment. The nitrogen activated in this way forms a layer which holds the caesium to the surface at comparatively high temperatures and thus increases the emission at these temperatures.

Adsorption of oxygen, nitrogen and hydrogen on tungsten.

I. Langmuir (*Journ. Amer. Chem. Soc.* xxxv. 105, 1913) has shown that oxygen causes a tremendous decrease in the emission from a tungsten filament; the adsorbed layer is decomposed at 1600° K. K. H. Kingdon (*Phys. Rev.* xxiv. 510, 1924) has found that the work function of such an oxygen-coated surface is 9·2 volts. Nitrogen has no effect on the emission unless it is activated by electron bombardment (Langmuir, *Phys. Zeit.* xv. 516, 1914). Hydrogen was found by Langmuir (*ibid.* xv. 516, 1914) to have no effect but H. Simon (*Zeit. f. tech. Phys.* v. 221, 1924) obtained an increase in the emission in the presence of hydrogen. A considerable amount of work has been done on the effect of hydrogen on the emission from platinum; early workers found a considerable increase in the emission when hydrogen was admitted but the effect is due to impurities on the surface (for a discussion of the effect of hydrogen on the emission from a platinum cathode see O. W. Richardson, *Emission of Electricity from Hot Bodies*, and W. Schottky, *Handbuch der exp. Physik*, xiii. pt 2).

Multiatomic adsorbed layers.

A study of multiatomic adsorbed layers on tungsten has been made by Ryde and Harris (Research Laboratories of the General

Electric Company, Wembley). Barium was distilled on a clean tungsten filament from an electrically heated spiral which surrounded it. The activation curve is similar to that for thoriated filaments. The Richardson equation is

$$I = 1{\cdot}5T^2e^{-\frac{18,100}{T}} \text{ amps per cm.}^2.$$

The value of the work function is about 1·56 volts. When about 85 % of the tungsten surface is covered by barium, the emission is only 1 % of that from the complete layer.

If a layer of oxygen is formed on the tungsten before the barium is deposited, the emission from WOBa is given by the equation

$$I = 0{\cdot}5T^2e^{-\frac{16,750}{T}} \text{ amps per cm.}^2,$$

and the work function for the double layer is about 1·4 volts.

As in the case of caesium, the rate of evaporation of barium is very much faster from the clean tungsten than from oxygen covered tungsten. For example, at 1250° K. the emission drops to half value in about 30 seconds in the case of WBa, while it takes over 100 hours with WOBa. In the latter case the oxygen layer is left practically complete after the barium has evaporated.

The distillation method enables observations to be made when a layer of oxygen is formed on top of the barium. In this case it is found that the equation for WBaO is

$$I = 1{\cdot}8 \times 10^{-2}T^2e^{-\frac{22,100}{T}} \text{ amps per cm.}^2,$$

and the work function becomes 1·9 volts.

If now the filament is held at about 1300° K. a remarkable reversal of the layers from WBaO to WOBa slowly occurs, without any appreciable loss of either oxygen or barium. After this reversal has taken place the rate of evaporation of the barium is practically the same as if the oxygen layer had been formed first and the barium deposited subsequently.

One oxygen atom appears to influence several neighbouring barium atoms: thus very incomplete layers of oxygen can produce a considerable reduction in thermionic emission and rate of evaporation. Also incomplete layers of oxygen may repeatedly be formed on WBa and allowed to reverse until no further oxygen can find a place below.

Nitrogen does not form an adsorbed layer on tungsten at these temperatures, but if the nitrogen is activated, either by a subsidiary filament or by the emission from the barium covered filament, it forms a layer on the barium and depresses the emission.

Nitrogen also possesses the interesting property of considerably accelerating the rate of reversal from WBaO to WOBa. For this it is not necessary for it to be in an activated state. Further, if the filament is cold, ordinary nitrogen forms an adsorbed layer on barium so that the surface is WBaN. In this state it is found that the barium is protected from oxygen. If the filament is now heated, the nitrogen comes off and WBaO is formed. If, however, the oxygen is removed before heating, the nitrogen layer comes off and the full thermionic emission of WBa is obtained immediately.

Perhaps one of the most remarkable results is that it has been found possible to build up systems of several alternating adsorbed layers of barium and oxygen. The two principal systems are:

(*a*) W O Ba O Ba O Ba ...

(*b*) W Ba O Ba O Ba O Ba ....

Of these, form (*a*) is very much more stable than (*b*). The former has been followed up as far as nine layers and the latter to six layers. The various layers of atoms in these multiatomic structures preserve a more or less individual existence and can be evaporated off or removed by nitrogen one by one. In thick films of barium oxide the barium ion at the surface diffuses back through the lattice of the oxide crystal until it reaches the underlying tungsten; here it obtains an electron and the newly formed barium atom wanders back to the outside, but only through the grain boundaries of the film. It is for this reason that microcrystalline emitting surfaces are better than large grained surfaces.

Oliphant (*Proc. Camb. Phil. Soc.* XXIV. 455, 1929) has studied the effect on the secondary electron emission of bombarding a metal surface with positive ions of the alkali metals. He found that with a target area of 3 mm. diameter and a positive ion current of 0·1 microampere it took almost eight minutes for the secondary electron emission to be constant, that is, on deposition of approximately four layers of atoms of sodium potassium and caesium, the nickel surface now behaves as one of pure alkali metal. With rubidium a film some seven atoms thick was necessary. In many cases, with low velocity positive ions, discharges can be effected and thick layers built up on the top of a gas film on the surface, but with high velocity positive ions this gas film can be broken down and the ions discharged on to the actual metallic surface. The evidence for the persistence of gas films, to which according to Oliphant the secondary electron emission may be due even at pressures as low as 10^{-8} mm., is in agreement with that noted on p. 201 and by Knefft (*Phys. Rev.* XXXI. 199, 1928).

Still another method has been elaborated for the investigation of the properties of unimolecular metallic films by Ives (*Astrophys. J.* LX. 4, 1924; *Phys. Rev.* XXXIV. 117, 1929), who has shown that the long wave limit of photoelectric emission of a metal in the form of a thin film varies with the film thickness. For a unimolecular film of an alkali metal on platinum this limit is farther towards the infra red end than the limit for a thick film of the same metal. The unimolecular film threshold value was found to be $0{\cdot}59\mu$ for sodium on platinum and tungsten, for potassium $0{\cdot}77\mu$, for rubidium $0{\cdot}795\mu$ and for caesium on platinum and on silver $0{\cdot}895\mu$.

These long-wave limits for the unimolecular films indicate that in contrast to thick layers the process of photoelectric emission occurs when sufficient energy is given to the atom to produce its first state of excitation, i.e. that the energy necessary to bring the atom to resonance releases the electron, and that there is no energy spent in overcoming the attractive action of the underlying metal because this is screened by the unimolecular film.

It might also be inferred that the unimolecular film of alkali metal is not adsorbed on the space lattice of the underlying platinum, but is either distributed at random or is in movement, otherwise the effects of the underlying metal lattice on the energy necessary for emission would not be negligible. We may observe that the work function of 9·2 volts found for oxygen on tungsten is in agreement with Ives' work on alkali films. The results might lead one to suspect that chemical reaction between an adsorbed atom and the substrate to form a heteropolar compound is a necessary preliminary to electron emission, and that such chemical reaction does not take place until the necessary energy of excitation has been provided from external sources; the following is a diagrammatic representation of this view:

$$\begin{array}{ccccccc} \mathrm{M} & & \mathrm{M} & & \mathrm{M} & & \mathrm{M} \\ \mathrm{MX} & \rightarrow & \mathrm{MX} & \rightarrow & \overset{+\,-}{\mathrm{MX}} & \rightarrow & \mathrm{MX} + \epsilon \\ \mathrm{M} & h\nu & \mathrm{M} & & \mathrm{M} & & \mathrm{M} \\ \mathrm{M} & & \mathrm{M} & & \mathrm{M} & & \mathrm{M} \end{array}$$

11. The heat of adsorption.

Some information on the properties of the solid gas interface may be obtained from an examination of the heats of adsorption of vapours and of gases.

If the available adsorbing surface remain constant in area during the process of adsorption of a vapour, then the affinity of the surface containing an amount x of adsorbed vapour for the liquid of the vapour will be given by

$$A_x = RT \log \frac{P_{\text{sat.}}}{P_x} \quad \text{....................(1)},$$

where P_x and $P_{\text{sat.}}$ are the respective partial pressures of the vapour above the adsorbent and the liquid. The heat of wetting λ_x can be determined with the aid of the Gibbs-Helmholtz equation

$$\lambda_x = A_x - T\left(\frac{\partial A_x}{\partial T}\right)_x = RT^2\left(\frac{\partial \log P_x}{\partial T}\right)_x - RT^2\frac{\partial \log P_{\text{sat.}}}{\partial T} \quad (2).$$

Williams (*Proc. Roy. Soc. Edin.* XXXVIII. 24, 1918) distinguishes between three isothermal heats of adsorption:

(*a*) The case where adsorption proceeds in such a manner that the vapour phase is continually in equilibrium with the adsorbed layer.

(*b*) The heat of adsorption at constant pressure in which the gas is at constant pressure but not necessarily the equilibrium pressure.

(*c*) The heat of adsorption at constant volume in which the total volume of the system is kept constant and the gas adsorbed with a fall of pressure. For gases which may be considered ideal and for an adsorbing surface which remains constant in area we obtain, as above for the heat of adsorption at constant pressure,

$$\lambda_{\text{P.T.}} = RT^2 \left(\frac{\partial \log P_x}{\partial T}\right)_x \quad\text{.....................(3).}$$

Calculations of the affinity have been made with a variety of surfaces for different vapours with the aid of equation (1). We may cite one from an extensive series of investigations by Goldmann and Polanyi (*Zeit. physikal. Chem.* CXXXII. 320, 1928) for the affinity of ethyl chloride for charcoal at – 15·3° C.

P_x mm.	$A_x = 1190 \log_{10} \frac{2436}{P_x}$ cals. per grm. mol
227·9	33
105·7	427
3·04	2243
1·41	2640
0·1193	3900
0·0372	4500
0·0177	4890

The heats of wetting calculated with the aid of equation (2) give values of approximately 5,000 cals. per grm. mol for the first grm. adsorbed on 10 grm. of charcoal, falling to 4,000 cals. when 1·5 grm. are adsorbed and 3,000 cals. on adsorption of 3·3 grm. In all cases when *ca.* 80 % saturation was attained a rapid rise followed by an abrupt fall in the heat of wetting was observed.

In a similar manner McHaffie and Lenher (*J.C.S.* CXXVII. 1559, 1925) have calculated the affinity of water for etched glass and for platinum with the results on p. 230.

Williams (*loc. cit.*) has compared the values for the heat of adsorption of ammonia determined by Titoff and those obtained with the aid of equation (3); the results are given on p. 230.

Glass			Platinum		
Temp. ° K.	Pressure	A_x cals. per grm. mol	Temp. ° K.	Pressure	A_x cals. per grm. mol
293	16·90	20·6	293·5	18·01	0
298	22·73	26·1	294	18·96	6·06
302	27·54	52·2	295	19·10	35·5
305	29·71	110·4	297	20·32	57·00
308	30·65	194·8	298	20·61	84·10
311	31·44	282·2			
314	31·97	374·1			
317	32·40	468·2			

Although Williams concluded that the lack of agreement was outside the range of the probable experimental error and that some other change such as expansion of the surface accompanied by heat evolution took place during adsorption, the difficulties of outgassing charcoal completely are so great that the discrepancies are probably unavoidable.

$\log_{10} x$ x in c.c. per grm. at N.T.P.	λ calc. cal. per c.c. at N.T.P.	λ obs. cal. per c.c. at N.T.P.
2·10	0·265	0·386
2·00	0·290	0·355
1·80	0·319	0·360
1·60	0·329	0·370
1·40	0·340	0·375
1·20	0·360	0·388
1·00	0·400	0·410
0·80	—	0·430
0·50	—	0·450

Lamb and Coolidge (*J.A.C.S.* XLII. 1146, 1920) have studied the heat of adsorption of a number of easily liquefiable vapours on charcoal. They showed that the heat evolved per grm. of charcoal λ was a function of the amount adsorbed expressible in the form $\lambda = ax^b$.

The following values were obtained for a and b with various vapours:

Vapour	a	b
CCl_4	0·893	0·930
$C_2H_5OC_2H_5$	0·917	0·921
CCl_3H	0·829	0·935
$HCOOC_2H_5$	0·944	0·907
CS_2	0·752	0·920
CH_3OH	0·742	0·938

They also arrived at the following conclusions:

(*a*) The greater the molecular volume the less adsorbable was the substance for a definite pressure and temperature.

(*b*) The greater the number of molecules adsorbed at a given pressure the smaller the heat of adsorption.

(*c*) Assuming the adsorbed gas to be in the liquid state, then the net heat of adsorption per c.c. of liquid was found to be identical for all substances examined, as indicated by the following data:

Substance	λ Heat evolved per grm. mol for adsorption of 1 c.c. of liquid per 10 grm. of charcoal. Cals.	L Molecular heat of vaporisation. Cals. per grm. mol	$\lambda - L$ Molecular net heat of adsorption	$\frac{\lambda - L}{V}$ Heat of adsorption per c.c. of liquid
CCl_4	16,090	6900	9190	85·6
C_2H_5Cl	12,330	6200	6110	86·4
C_6H_6	15,170	7810	7360	85·0

The variation in the heat of adsorption of ammonia by meerschaum has been likewise examined by Chappuis (*Wied. Ann.* XIX. 21, 1883) and the data are given overleaf.

Conclusions similar to those of Lamb and Coolidge for the heat of adsorption of a number of vapours and of some gases were arrived at by Gregg (*J.C.S.* II. 1506, 1927), although in the case of nitrogen the exponent *b* was found to be almost unity. The Williams equation was found to be generally applicable.

Kälberer, Mark and Schuster (*Zeit. Elektrochem.* XXXV. 601, 1929) have calculated the "heats of adsorption" by assuming

Pressure cm. Hg	λ cals. per grm. mol.
0	20,500
0 – 0·5	12,700
0·5– 3·7	11,300
2·9–21	8,970
21 –57	7,600
Heat of liquefaction	5,000

them to be identical with the change in potential energy derived from the adsorption isotherms by means of a modification of the Boltzmann equation given on p. 71.

$$\frac{\Delta n_1}{\Delta n_2} = \frac{p_1}{p_2} \frac{A\delta - n_1 v}{V} e^{\frac{\phi}{kT}}.$$

They neglect the volume $n_1 v$, thus obtaining

$$\frac{x}{p} = \frac{A\delta}{V} e^{\frac{\phi}{kT}},$$

and calculate the following values:

SILICA GIL.

Gas	ϕ cals. per grm. mol	Temp.° K.	$A\delta \times 10^4$	A cm.$^2 \times 10^4$
C_2H_4	7100	273	2·5	1·7
CO_2	7200	273	2·49	1·66
CO	5300	348	45	30
N_2	3000	273	72·4	48
A	2500	273	174	110

ALUMINIUM OXIDE.

Gas	ϕ at 0° C. cals. per grm. mol	$A\delta \times 10^4$	A cm.$^2 \times 10^4$
A	1800	468	300
CH_4	2200	490	320
C_2H_6	4900	29·5	20
C_2H_4	6400	3·99	2·7
Propane	6500	13·5	9·0
Propylene	9500	0·27	0·18

Whilst for the more perfect gases the $\log \frac{x}{p}, \frac{1}{T}$ curves are linear over a wide range, for more condensible and thus more readily adsorbable gases, e.g. C_2H_2, NH_3, the curvature is more pronounced in the sense that the apparent value of $A\delta$ decreases with increasing surface concentration; this is as might be anticipated, for at high surface concentrations the volume occupied by the molecules is not negligible, and at the same time (Ch. XI) it is possible that the potential function ϕ changes with the closeness of packing of readily polarisable gases and vapours.

The investigations of the heats of adsorption both of carbon dioxide and of oxygen on charcoal at low pressures have led to somewhat different conclusions. Magnus (*Zeit. anorg. Chem.* CLI. 140, 1926; *ibid.* CLXIV. 345, 357, 1927) and his co workers have shown that at pressures above 100 mm. the heat of adsorption of carbon dioxide falls but slightly with the pressure, the following table showing the variation observed at two different temperatures:

Temperature	Pressure in mm.		
	194	417	444
	cals. per grm. mol	cals. per grm. mol	cals. per grm. mol
17° C.	7740	7514	7487
37° C.	7662	7407	7376

At low pressures however the heat of adsorption rises, the rapid rise commencing at 40 mm. and attaining a value of 12,450 cals. at a pressure of 0·076 mm.

Blench and Garner (*J.C.S.* CXV. 1288, 1924), Keyes and Marshall (*J.A.C.S.* XLIX. 164, 1927) and Ward and Rideal (*J.C.S.* CXXIX. 3117, 1927) obtained initial heats of adsorption for oxygen as high as 72,000 cals. per grm. mol at 0° C., sinking rapidly to the almost constant value of *ca.* 4,000 cals. per grm. mol after *ca.* 2 c.c. per grm. had been adsorbed. The heat of adsorption at low pressures was found by the former investigators to possess an extremely large positive temperature coefficient rising to some 224,000 cals. per grm. mol at 450° C., approximating to the heat of formation of carbon dioxide from gaseous carbon, viz. 400,000 cals.

Keyes and Marshall state that they found an initially large heat of adsorption for chlorine and for ammonia, but the effects were not as marked as for oxygen. Titoff (*Zeit. physikal. Chem.* LXXIV. 641, 1910) obtained 8,350 cals. per grm. mol for the first 0·316 c.c. of hydrogen adsorbed on charcoal, with a subsequent value of 4,500 cals./grm. mol up to 14 c.c. adsorbed; for ammonia for the first 6 c.c. 11,270 cals./grm. mol. and then a constant value of 8,000 cals./grm. mol up to 120 c.c. adsorbed.

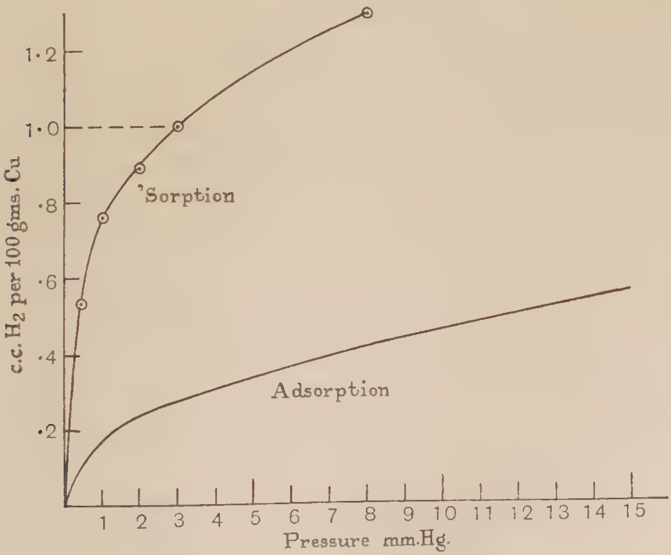
Heats of adsorption on metals.

The evidence for high initial heats of adsorption on metals is less conclusive. Foresti (*Gaz. Chim. Ital.* LIII. 487, 1923) obtained 11,400 cals./grm. mol for hydrogen on active nickel in agreement with a calculated value of 12,000 cals./grm. mol (Rideal, *J.C.S.* CXXI. 309, 1922); Beebe and Taylor (*J.A.C.S.* XLVI. 43, 1924) values from 13,500 to 20,500 cals./grm. mol dependent on the previous treatment of the sample.

For hydrogen on copper Beebe and Taylor obtained 9,600 cals./grm. mol, and for carbon monoxide on copper Beebe (*J.P.C.* XXX. 1538, 1926) obtained an initial high heat of from 20,000 to 30,000 cals./grm. mol which fell after 2–3 c.c. were adsorbed to about 9,000 cals. per grm. mol. Fryling (*J.P.C.* XXX. 818, 1926) with different copper catalysts found heats varying from 8,000 to 30,000 cals./grm. mol. Whilst the initial heats were large, some promoted catalysts gave an initial low heat before the region of high heat. Taylor and Kistiakowsky (*Zeit. physikal. Chem.* CXXV. 341, 1927) and Kistiakowsky, Flosdorf and Taylor (*J.A.C.S.* XLIX. 2200, 1927) repeated the work and also found an initial low heat of adsorption. Dew and Taylor (*J.P.C.* XXXI. 277, 1927) obtained 16,000–8,000 cals. per grm. mol, 11,300–6,000 cals. per grm. mol and 8,700 cals. per grm. mol for the heat of adsorption of ammonia on iron, nickel and copper per grm. mol, the lower values being obtained near the saturation point.

Taylor gives values for the heat of adsorption of carbon monoxide on copper of 30,000, sinking to 11,750 cals. per grm. mol as saturation is approached. On platinum black Kistiakowsky obtained some 100,000 cals. per grm. mol for the heat of adsorption of oxygen, 32,400 for hydrogen, 38,600 for carbon monoxide and 35,700 for sulphur dioxide.

The experiments of Ward make it probable that the initial low heats of adsorption occasionally obtained are due to solution of the gas in the metal occurring simultaneously with adsorption. For active catalysts at low pressures, when the interior of the solid is almost devoid of dissolved gas, the quantity entering into solution in three minutes in sixty grams of copper is comparable with the amount adsorbed. Since the heat of solution of hydrogen in copper is probably slightly endothermic at room temperatures (Sieverts, *Zeit. physikal Chem.* XL. 179, 1907; *Ber.* XLIII. 893, 1910; *Zeit. physikal. Chem.* LXXVII. 591, 1911), *ca.* 3,000 cals. per grm. mol, low apparent heats of adsorption will be obtained until higher pressures are reached, when the rate of solution in the gas containing solid becomes a less important factor.



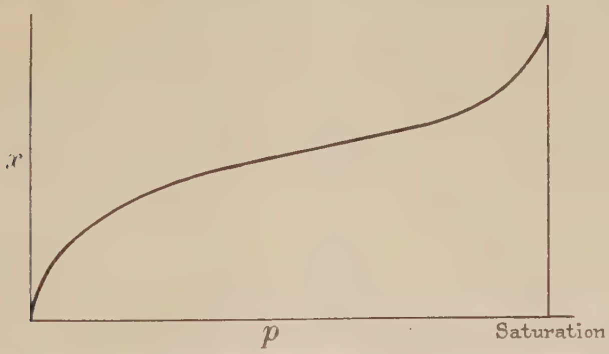
The sorption and adsorption curves obtained by Ward for hydrogen and copper are depicted above. The former is naturally not the equilibrium curve, but represents the amount of gas entering the metal during the time intervals necessary for the calorimetric observations. On determining the heats of adsorption on copper, Ward found that the heat of adsorption was constant at all stages of filling the surface but varied with the age of the surface. On a freshly prepared copper surface the heat of adsorption was found to be some 56,000 cals. per grm. mol, rapidly dropping to 26,500 cals. per grm. mol on increasing age, and finally settling down to a constant value of *ca.* 14,000 cals. per grm. mol.

12. Adsorption on rough surfaces.

The wide difference between the views of Langmuir and Volmer on the one hand and of Eucken and Polanyi on the other necessitates a closer analysis of the experiments which have been advanced to support the two theories. We may first enquire whether there is any definite evidence for the formation of multimolecular layers of gases or even vapours when on plane surfaces. The data of Langmuir for adsorption of gases on platinum and mica definitely negative the view that multimolecular layers are formed. Similar conclusions can be drawn from the work of Iredale (see p. 76) on the adsorption of vapours on liquid mercury and from the behaviour of lenses of benzene on water. Vapour condensing in excess of that required for the formation of a unimolecular layer collects into a lens and does not accumulate in the form of a sheet of increasing thickness.

McHaffie and Lenher (*J.C.S.* CXXVII. 1559, 1925), Lenher (*J.C.S.* CXXVIII. 1785, 1926; CXXIX. 272, 1927) and Frank (*J. Phys. Chem.* XXXIII. 970, 1929) concluded from their experiments on the adsorption of water and benzene vapour on glass fused quartz and platinum that thick films were formed. Smith (*J.C.S.* CXXX. 2045, 1928) arrived at similar conclusions for the adsorption of these vapours on amalgamated platinum. On the other hand, on freshly blown glass Frazer, Patrick and Smith (*J. Phys. Chem.* XXXI. 897, 1929) obtained no evidence for multimolecular adsorption; this was also found to be the case for smooth amalgamated silver by Latham (*J.A.C.S.* L. 2987, 1928), and for pyrex glass with toluene vapour by Carver (*J.A.C.S.* XLV. 45, 1923).

If glass be etched either with acids or even on standing in contact with water, or if a metal surface be made rough, then quantities of vapour in excess of the quantity apparently necessary for the formation of a unimolecular layer are readily taken up. The evidence against multimolecular layer formation for gases and vapours (up to the dew point) on plane surfaces may be regarded as convincing*, and it remains to investigate how far the quantities of gases and vapours taken up by porous and rough surfaced materials may be reconciled with the view that first a unimolecular is in reality formed but owing to gross undervaluation of the specific surface the apparent adsorption is greater. An examination of the complete adsorption isotherms for vapours up to the saturation point indicates that the isotherm is composite, the first portion obeying quite closely the adsorption isotherm of Langmuir or, up to 40 % saturation, with that of Williams†, but as the pressure increases more



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* We may note that on metals the question whether adsorbed gases occupy only the intrinsic field volume or both the intrinsic field volume and the first layer of the mirror image field remains open. It is possible in experiments on adsorption that only in rare cases is the intrinsic field ever completely denuded of material.

† Williams makes, as we observed, no assumption as to the thickness of the adsorbed layer; by extrapolation he calculated the constants of the zero isostere and from these obtained the area of the surface and the thickness of the film. From Homfray's data on charcoal the surface area was found to be $1{\cdot}3 \,.\, 10^6$ cm.^{2} per grm. and the thickness of the film 3·2 to 4·1 Å., i.e. a unimolecular layer. The Williams equation also holds true for O_2 and H_2 on silica gel and for N_2 and H_2 on charcoals up to a pressure of 100 atmospheres. (Briggs, *Proc. Roy. Soc. Edin.* XLI. 119, 1921.) (See also H_2O on oxides, Bray and Draper, *Proc. Nat. Acad. Sci.* XII. 297, 1926.)

vapour is taken up. We may conclude with some degree of assurance that a unimolecular layer is first formed over the whole of the accessible area, but that at higher pressures an excess of vapour is adsorbed in excess of the unimolecular saturation amount. The most striking result of the numerous investigations on the adsorption of vapours on rough materials is that with the vapours of different liquids the material, usually charcoal, shows an almost fixed adsorption volume rather than a fixed adsorption area. Some values taken from the accurate data of Coolidge (*J.A.C.S.* XLVIII. 1795, 1926) are given below.

Vapour	Volume of liquid at 0° C. necessary to give the volume of vapour required for saturation of 1 grm. charcoal at 0° C.
H_2O	0·424
CCl_4	0·434
$CHCl_3$	0·442
CS_2	0·450
CH_3OH	0·450
$HCOOC_2H_5$	0·454
C_6H_6	0·467
CH_3COOCH_3	0·490
$(C_2H_5)_2O$	0·490

These values are not completely concordant and the discrepancy has been ascribed to one of two causes, either water penetrates not so deeply as ether into the narrowest of the micropores, thus saturation is obtained at a lower apparent adsorptive volume, or the vapour when condensed is subjected to high pressures, for the saturation volumes of the liquids stand almost in the order of their compressibilities. Whilst a definite decision on this point has not been attained, yet the view that condensation occurs receives strong support.

According to the classical view, condensation in the capillaries of the porous materials would occur above the dew point of the liquid on account of their small size. This theory of capillary condensation has been supported by Zsigmondy (*Zeit. anorg. Chem.* LXXI. 356, 1911; *Zeit. physikal. Chem.* LXXV. 189, 1912), Anderson (*Zeit. phys. Chem.* LXXXVIII. 213, 1914) and Patrick and his co-workers (*J.A.C.S.* XLII. 946, 1920; *Koll. Zeit.* XLI. 272, 1925; *J.P.C.* XXIX. 336, 1926; *ibid.* XXIX. 421, 1926; *ibid.* XXIX. 601, 1926).

If the Kelvin equation be applied for determining the sizes of the capillaries which would be filled with liquid for the different pressures observed on the adsorption isotherm, the radii are found to be less than the molecular diameters at low pressures and increase in size up to five or six molecular diameters as the pressure increases. We have already noted the experimental evidence against the applicability of the Kelvin equation to such micropores, and the theory of capillary condensation in this form can be criticised as shown by Coolidge and Polanyi in other directions. In the first place the temperature coefficient of absorption is far less than is that demanded by the capillary theory, in fact the quantities of vapour calculated as liquid required to saturate charcoal with rising temperatures is about that calculated from the coefficient of dilation. Coolidge obtained the following data:

Liquid	Temperature range ° C.	Ratio of volumes in liquid form condensed at the two temperatures at the saturation point	Ratio of volumes of liquid at the two temperatures from coefficient of dilation
Benzene ...	33–99	1·065	1·09
Ether	0–60	1·09	1·11
Carbon disulphide	0–60	1·07	1·08
Methyl alcohol ...	0–60	1·08	1·07
Water	0–99	1·05	1·04

The absorbed water showed a regular coefficient of dilation.

Coolidge has tested the Kelvin equation from the relative pressures of different vapours required to fill a gram of charcoal with the same amount of vapour, i.e. 0·2 c.c. in the condensed form at 0° C. In the case of benzene at 0° C. the pressure necessary was 0·0055 mm. With a value of $\sigma = 32$ dynes per cm. and $v = 86{\cdot}9$ c.c., we obtain $r = 2{\cdot}89$ Å. as the mean radius of the capillaries. Taking the relative pressures for different liquids, he obtains:

	Benzene		CS_2	Ether	Water
Liquid temperature ° C.	99	150	0	0	0
$-\log p$ calc.	1·82	1·19	2·65	2·51	1·80
$-\log p$ obs.	2·74	2·44	2·60	4·00	0·26

The same lack of agreement is found in the data of McGavack and Patrick (*loc. cit.*) for the absorption of sulphur dioxide by silica gel. We may note that in these investigations Coolidge ignores the possibility of a variation in the wetting angles of these different liquids for the charcoal surface. The evidence presented leads to the conclusion that there exist three stages in the filling of a porous solid with vapour—the formation of a unimolecular layer, the filling of microcapillaries and finally the filling of macrocapillaries. The Kelvin equation is not applicable to the filling of the microcapillaries and it appears that no simple equation has yet been developed connecting p and x over this range.

The evidence for lateral mobility of the surface adsorbed phase has already been presented, but as was noted, whilst the visual observation of the migration of adsorbed metal atoms on various surfaces have been obtained, it is doubtful whether the adsorbed atoms were moving over the adsorbent or over a gas film already present in the adsorbent. The work of Davisson and of Germer (*loc. cit.*) leads us to suspect that on nickel at any rate adsorbed gases are not readily removed, a result quite readily understood if the gas were oxygen.

In the Langmuir isotherm $x = \dfrac{abp}{1 + ap}$ the factor b represents the surface saturation maximum, and the applicability of the isotherm has been criticised by Polanyi since b should not vary with the temperature but in fact does so. The criticism is not quite valid since there will be a coefficient of superficial dilation of the solid, the number of elementary spaces per sq. cm. decreasing with elevation of the temperature; further, the fissures in the grain boundaries may suffer quite considerable changes in size with alteration in the temperature. Zeise (*Zeit. physikal. Chem.* CXXXVIII A. 289, 1928) has calculated the values of b for various temperatures from the experimental data of Homfray, Titoff and Richardson, and finds that over a wide range b can be expressed in the form $b = b_0 - kT$.

If $\frac{db}{bdT}$ be calculated from his figures, a value much greater than that attributable to the increase of superficial area due to thermal expansion alone, i.e. *ca.* ·00001, is obtained.

On the other hand if the adsorbed phase is not rigid, we might regard, with Wilkins and Ward (*Zeit. physikal. Chem.* CXLIV A. 259, 1929), the adsorption maximum occurring at a constant value of the two-dimensional pressure. The area per grm. mol, $1/b$, at saturation will therefore increase with temperature in a manner similar to the expansion of a gas at constant pressure and the saturation maximum will decrease. The coefficient $\frac{db}{bdT}$ should be equal to the cubical expansion of a gas, i.e. 0·0037 at 0° C. for a perfect gas.

Some of the values for $\frac{db}{bdT}$ are given in the following table.

Observer	Gas	Adsorbent	Mean temp. ° C.	$-\frac{db}{bdT}$
Titoff	N_2	Charcoal	0	·0059
	NH_3	,,	0	·0057
Richardson	NH_3	,,	0	·0031
	CO_2	,,	0	·0051
Homfray	Ar	,,	0	·0080
	CO	,,	0	·0094
Gutbier and Maisch	H_2	Pt black	0	·0027
Geddes	CO_2	Charcoal	25	·0085
Firth	NH_3	,,	0	·0086
Travers	CO_2	,,	40	·0010
Langmuir	N_2	Mica	– 150	·0146
	CH_4	,,	– 150	·0193
	CO	,,	– 150	·0150
	A	,,	– 150	·0145
	O_2	,,	– 150	·0195

It will be observed that the values of $\frac{db}{bdT}$, although subject to wide variations, are of the same order as the coefficient of dilation of a two-dimensional gas, the gas becoming more imperfect as the temperature is lowered. The two-dimensional pressures are of course unknown and probably vary from gas to gas.

This examination of the effect of temperature on the saturation maximum of the unimolecular film supports the concept of a mobile rather than a static two-dimensional phase.

13. The rate of surface attack.

Two different types of surface attack by gases can be considered; in one the product of reaction is rapidly volatilised from the surface so that the surface is always clean; in the other the product is non-volatile and the reactant diffuses through an increasing thickness of product.

But little attention has been paid to the former class of reactions, although the rate of oxidation of tungsten by Langmuir (*J.A.C.S.* XXXVII. 1161, 1915), of platinum by Rideal and Wansbrough Jones (*Proc. Roy. Soc.* A, CXXIII. 214, 1929) and the rate of chlorination of copper by Frommer and Polanyi (*Zeit. physikal. Chem.* CXXXVII. 201, 1928) have been studied under these conditions. From the influence of the temperature on the reaction rate, which is given by

$$\frac{dx}{dt} = KpA\,e^{-\frac{E}{RT}},$$

where A is the accessible area and p the pressure of the gas which is very low, the energies of activation can be determined. In the case of the oxidation of these two metals they are found to be $E = 20,000$ and $E = 63,000$ cals. per grm. mol respectively. The data for the chlorination of copper are not sufficiently comprehensive for an accurate evaluation of E, but it is certainly small. A close parallelism is to be noted between the critical energy increments and the electron work functions of the metal as is indicated by the following data.

Metal	E volts	ϕ volts	$\phi - E$
Pt	2·74	6·35	3·61
W	0·87	4·48	3·61

We might anticipate that metals with work functions less than 3·61 volts would undergo oxidation without energy of activation, thus forming reactions of the class usually defined as elementary reactions.

The formation of relatively thick films on metals by surface attack has been studied at low temperatures chiefly by Tammann (*Zeit. anorg. Chem.* CXXIII. 197, 1923; CXXVIII. 179, 1923; CLII. 149, 1926; CLXIX. 43, 1927), Evans and Bannister (*Proc. Roy. Soc.* A, CXXV. 370, 1929) and Kohlschütter (*Zeit. Elektrochem.* XXIX. 570, 1923), and at higher temperatures by Pilling and Bedworth (*Journ. Inst. Metals*, XIX. 529, 1923), Utida and Saito (*Sci. Rep. Tohoku Univ.* XIII. 391, 1925) and by Dunn (*Proc. Roy. Soc.* A, CXI. 211, 1926). When the volume of the oxide is less than the volume of metal from which it is formed, a porous non-protective oxide is formed; such is the case with the alkali and alkaline earth metals. Other metals form compact films both with oxygen and with the halogens.

The rate of attack by these gases at relatively high pressures is given by the parabolic diffusion law

$$x^2 = kt + c \quad \text{........................(1)},$$

where x is the thickness of the oxide film formed. It is clear that the gas must diffuse either through the lattice of the oxide or halide or along the grain boundaries (see Rolf, *J. Inst. Met.* XXIX. 587, 1927), i.e. in the Smekal cracks contained in the film. In special cases, e.g. zinc in the case of the oxidation of brass (Dunn, *loc. cit.*) or, according to Pfeil (*J. Iron and Steel*, CXIX. 500, 1929), iron in the high temperature oxidation, the metal may diffuse up through the layer of oxide to meet the entering gas.

The relative extents to which lattice diffusion or grain boundary diffusion of the gas through the protecting film takes place depends on the nature of the film and the temperature. Investigations on the rate of oxidation of copper have been extended by Hinshelwood (*Proc. Roy. Soc.* A, CII. 318, 1922), and by Wilkins; the latter concludes that at high temperatures both lattice and grain boundary diffusion takes place, but at temperatures below 600° C. the grain boundary diffusion process is predominant.

It was found that with copper which had been activated, by alternate oxidation and reduction, the initial rate of oxidation as measured by the decrease in pressure of the gas exposed to the metal could be expressed in the form

$$\log \frac{p_0}{p} = kt \quad \dots\dots\dots\dots\dots\dots\dots (2).$$

This simple relationship does not hold when the oxygen pressure is high or when the specimen of copper had not been rendered active by the process of alternate oxidation and reduction. The four factors which have to be considered in the attack of a metal through a film of product, e.g. oxide by a gas such as oxygen, are (*a*) the rate of supply of oxygen to the oxide surface, (*b*) the rate of removal of the oxygen from the oxide surface into the gas by evaporation and into the oxide by penetration, (*c*) the rate of diffusion of the oxygen which has penetrated into the oxide and (*d*) the final rate of reaction with the metal. The evidence presented in the previous section shows that this latter reaction is, for all metals with low electron work functions, a relatively rapid process. At low pressures (*a*) will be the controlling factor, and under these circumstances we obtain

$$-\frac{dp}{dt} = kp \quad \dots\dots\dots\dots\dots\dots\dots (3),$$

giving on integration (2) conditions experimentally realised by Wilkins.

On inactive copper the grain size is large and the diffusion rate (*c*) is thus the controlling factor. The temperature coefficient of the low temperature oxidation was found to be 10,000 cals. per grm. mol; this low value suggests that it is nothing more than the energy which a portion of the grain boundary must possess before an oxygen molecule can diffuse.

Since the preliminary to reaction is an adsorption on the surface of the oxide film, it is evident that the parabolic law will hold only for conditions under which the adsorbing surface is saturated. The surface adsorption equilibrium will depend at low temperatures both on the gas pressure as well as on the number of Smekal cracks through which the gas can pass by lateral diffusion; thus we anticipate a limiting pressure above which the quadratic diffusion law is obeyed and that this limiting pressure should vary with the activity of the surface, being higher for active surfaces. Pilling and Bedworth (*loc. cit.*) obtained 0·3 mm., Berger (*C.R.* CLVIII. 1502, 1798, 1914) 100 mm. Wilkins obtained 9·5 mm. for inactive copper, rising to 25·2 mm. after the first process of activation, 60 mm. after three more alternate oxidations and reductions, and finally 130 mm. after eight such alternate processes. On sintering the metal oxide, the limiting pressure was reduced again.

If ν_g be the rate of evaporation of oxygen from the oxide surface and ν_s the rate of penetration into the oxide from unit area and a fraction θ of the surface is covered when the pressure is p, then the rate of condensation of the gas on the oxide surface will be

$$akp\,(1-\theta) \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4),$$

the rate of loss from the oxide surface into the gas phase and into the solid will be

$$(\nu_g+\nu_s)\,\theta \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5).$$

A further loss, important near the limiting pressure where θ approaches unity, may result by evaporation caused by an adsorbed molecule being struck by a molecule from the gas phase; this can be written

$$\nu p\theta \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6).$$

The rate at which the surface attains equilibrium will be given by the relative rates of the above three processes or

$$\begin{aligned}\frac{d\theta}{dt} &= akp\,(1-\theta)-(\nu_g+\nu_s)\,\theta-\nu p\theta\\ &= ap\,(1-b\theta)-c\theta,\end{aligned}$$

where a, b and c are constants.

At equilibrium $\frac{d\theta}{dt}=0$ or $ap\,(1-b\theta)-c\theta=0$, and since

$$-\frac{dp}{dt}=\frac{k\theta}{p_0-p},$$

we obtain

$$-\frac{dp}{dt}=\frac{Kp}{(p_0-p)\,(Kp+k_1)} \quad\text{and}\quad P_{\text{limiting}}=\frac{(\nu_g+\nu_s)\,\theta}{ak\,(1-\theta)-\nu\theta},$$

which increases with the number of grain boundaries (ν_s) present per unit area.

Wilkins found that this expression held accurately for the reaction rate after the surface equilibrium had been attained.

He likewise noted an interesting phenomenon in that electrostatic fields of the order only of 30–40 volts per cm. altered the high pressure but not the low pressure oxidation rate of copper. As we have seen (p. 208), only high field strengths could alter the adsorptive equilibrium which governs the low pressure oxidation rate; this effect must therefore be due to the influence of a charge on the rate of diffusion of oxygen through the Smekal cracks, possibly effected by altering the spacing between the blocks forming the grains, but a detailed investigation of this phenomenon would be desirable.

14. Catalytic reactions at solid surfaces.

Many solid surfaces are the seat of catalytic action (cf. Sabatier, *La Catalyse en Chimie Organique*; Rideal and Taylor, *Catalysis in Theory and Practice*).

In considering the reaction velocity as a function of the partial pressures, both those of the reactants and frequently those of the products have to be considered.

For the purposes of classification it is convenient to regard the reactions taking place as two-dimensional gas reactions on the surface, the rates being proportional to the surface concentrations. In the case of a bimolecular reaction, partial inhibition takes place when the reactants are not adsorbed in the optimum ratio; if the product is strongly adsorbed, the reaction velocity will likewise suffer a fall.

The relationship between the surface concentration and the gas pressure can be expressed with the aid of the suitable adsorption isotherm. A convenient classification of surface reactions has been given by Schwab (*Ergeb. der Deut. Naturwiss.* VII. 276, 1928) and by Schwab and Pietsch (*Zeit. Elektrochem.* XXXV. 575, 1929). On the assumption of the applicability of the Langmuir isotherm,

$$x = \frac{abp}{1 + bp},$$

the surface concentration will be proportional to the gas pressure at low pressures or for gases weakly adsorbed, and independent of the gas pressure at high pressures or for gases strongly adsorbed.

The table of these authors with slight modification is given below.

TYPE A. Decomposition of a reactant R at a pressure p at a surface, the products exerting no inhibiting effect.

Case	Reaction velocity as a function of the pressure of R	Example	Surface
A 1. R weakly adsorbed	$-\frac{dR}{dt} = kp$	AsH_3, PH_3 HCOOH CH_4	Glass[1] Various surfaces[2] Carbon[3]
A 2. R fairly strongly adsorbed	$-\frac{dR}{dt} = \frac{kp}{1+bp}$	SbH_3 NH_3	Glass[4] Tungsten[5]
A 3. R strongly adsorbed	$-\frac{dR}{dt} = k$	HI	Gold[6]

TYPE B. Decomposition of a reactant R at a pressure p at a surface, one product B at a partial pressure p' inhibiting the reaction.

Case	Reaction velocity as a function of the pressure of R and of B	Example	Surface
B 1. R weakly adsorbed but B fairly strongly adsorbed	$-\frac{dR}{dt} = kp . \frac{1}{1+b'p'}$	N_2O	Platinum[7]
B 2. R weakly adsorbed but B very strongly adsorbed	$-\frac{dR}{dt} = kp . \frac{1}{p'}$	NO	Platinum[8]
B 3 i. Both R and B strongly adsorbed	$-\frac{dR}{dt} = \frac{kp}{1+bp+b'p'}$ or if $bp \geqslant 1 = \frac{kp}{bp+b'p'}$	NH_3 at low pressures	Platinum[9]
B 3 ii. R weakly adsorbed but two products B and C strongly adsorbed	$-\frac{dR}{dt} = \frac{kp}{b'p' + b''p''}$	NH_3	Platinum[9]

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[1] Van't Hoff and Kooj, *Zeit. physikal. Chem.* XII. 185, 1893.

[2] Hinshelwood and Topley, *J.C.S.* CXXIII. 1014, 1923.

[3] Schwab and Pietsch, *Zeit. physikal. Chem.* CXXI. 189, 1926; CXXVI. 473, 1927; *Zeit. Elektrochem.* XXXII. 430, 1926; Bone and Coward, *J.C.S.* XCIII. 1197, 1908; Cantelo, *Zeit. physikal. Chem.* CXXX. 899, 1926.

[4] Stock and Bodenstein, *Ber.* XL. 570, 1907.

[5] Hinshelwood and Burk, *J.C.S.* CXXVII. 1105, 1925.

[6] Hinshelwood and Pritchard, *J.C.S.* CXXVII. 1552, 1925.

[7] Hinshelwood and Pritchard, *J.C.S.* CXXVII. 327, 1925.

[8] Hinshelwood and Green, *J.C.S.* CXXVIII. 1709, 1926.

[9] Hinshelwood and Burk, *J.C.S.* CXXVII. 1105, 1925.

TYPE C. A multimolecular reaction $nR + mS \rightarrow B + \ldots$ in which the products do not inhibit the reaction.

Case	Reaction velocity as a function of the pressure of R and of S	Example	Surface
C 1. Weak adsorption of both R and S	$-\frac{dR}{dt} = kp_R^n p_S^m$	$2H_2 + O_2 \rightarrow 2H_2O$ $C_2H_4 + Br_2 \rightarrow C_2H_4Br_2$	Porcelain[10] Glass[11]
C 2. R weakly adsorbed, S fairly strongly adsorbed	$-\frac{dR}{dt} = k\left(\frac{p_R}{1 + b_S p_S}\right)\left(\frac{p_S}{1 + b_S p_S}\right)$	$CO_2 + H_2$	Platinum[12]
C 3. R weakly adsorbed, S strongly adsorbed	$-\frac{dR}{dt} = \frac{kp_R}{p_S}$	$2H_2 + O_2$ at low temperatures $2CO + O_2$ $C_2H_4 + H_2$	Platinum[13] Platinum[13] Copper[14]
C 4. R very weakly adsorbed, S strongly adsorbed	$-\frac{dR}{dt} = kp_R$	$2H_2 + O_2$ at high temperatures $2CO + O_2$	Platinum[13] Platinum[13]

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[10] Bodenstein, *Zeit. physikal. Chem.* XXIX. 665, 1899.

[11] Steward and Edland, *J.A.C.S.* XLV. 1914, 1923.

[12] Hinshelwood and Pritchard, *J.C.S.* CXXVII. 1552, 1925.

[13] Langmuir, *Trans. Farad. Soc.* XVII. 621, 1922.

[14] Rideal, *J.C.S.* CXXI. 309, 1922.

TYPE D. A multimolecular reaction $nR + mS \rightarrow B + \ldots$ in which a product inhibits the reaction.

The contact process for the formation of sulphur trioxide on platinum black examined by Bodenstein and Fink (*Zeit. physikal. Chem.* LX. 1, 1907) is the only reaction examined which falls in this class; the reaction velocity can be expressed in the approximate forms with excess of either reactant

$$-\frac{dR}{dt} = \frac{kp_R}{1 + p_B} \quad \text{or} \quad -\frac{dR}{dt} = \frac{kp_S}{1 + p_B}.$$

A few other reactions have been examined, but not in great detail, which do not fit into this scheme.

From the influence of temperature on the reaction velocity we can calculate the energies of activation according to the following method due to Kunsman.

If a_i be the rate of condensation of one of the participatory gases, and σ_i the fraction of the surface covered with the gas i, the rate of evaporation of this gas i at a temperature T will be

$$b_i e^{-\frac{\lambda_i}{RT}},$$

where λ_i is regarded as a constant; hence

$$B_i = a_i^{-1} b_i e^{-\frac{\lambda_i}{RT}},$$

$$\frac{dB_i}{dT^{-1}} = \frac{\lambda_i B_i}{R}.$$

When equilibrium with the surface is established

$$\left(1 - \sum_0^n \sigma_i\right) a_i = \sigma_i b_i e^{\frac{\lambda_i}{RT}} \quad (i = 0, 1, 2, \ldots),$$

i.e.

$$\sigma_0 (1 + B_0) + \sigma_1 + \sigma_2 + \ldots + \sigma_n = 1,$$

$$\sigma_0 + \sigma_1 (1 + B_1) + \sigma_2 + \ldots + \sigma_n = 1,$$

$$\sigma_0 + \sigma_1 + \sigma_2 + \ldots + \sigma_n (1 + B_n) = 1.$$

Solving these equations for σ_0, σ_1, σ_2, etc.,

$$\sigma_i = \frac{B_0}{AB_i} \quad (i = 0, 1 \ldots n),$$

where

$$A = 1 + B_0 + \frac{B_0}{B_1} + \ldots + \frac{B_0}{B_n}.$$

If the forward reaction has an observed reaction velocity of k with a true heat of activation Q, then

$$k \propto \sigma_0 e^{-\frac{Q}{RT}},$$

$$\frac{d}{dT^{-1}} \log k = -\frac{E}{RT} = -\frac{Q}{R} + \frac{d}{dT^{-1}} \log \sigma_0,$$

and E the observed heat of activation is equal to

$$\begin{aligned} Q - R\frac{d}{dT^{-1}} \log \sigma_0 &= Q + R\frac{d}{dT^{-1}} \log A \\ &= Q + RA^{-1}\frac{dA}{dT^{-1}} \\ &= Q - A^{-1}\left\{\lambda_0 B_0 + \sum_1^n (\lambda_0 B_0 - \lambda_1 B_0) B_0^{-1}\right\} \\ &= Q - A^{-1}\left\{\lambda_0 (A - 1) - B_0 \sum_0^n \lambda_i B_i^{-1}\right\} \\ &= Q - \lambda_0 (1 - \sigma_0) + \lambda_1 \sigma_1 + \lambda_2 \sigma_2 + \ldots + \lambda_n \sigma_n \\ &= Q - \lambda_0 + \sum_0^n \lambda_i \sigma_i. \end{aligned}$$

If λ_i are all equal and the surface is completely covered, $\Sigma\sigma_1 = 1$, then $E = Q$; again if λ_i are all about equal and $\Sigma\sigma_1$ is constant, E will be constant.

We can apply this to the case of the decomposition of ammonia into nitrogen and hydrogen on the surface of metals; the ammonia is adsorbed on a fraction of the surface σ_0, the product hydrogen on a fraction σ_1, and the nitrogen is only very weakly adsorbed. Thus we obtain

$$(1) \quad \sigma_0 + \sigma_1 = 1,$$

$$(2) \quad \frac{\sigma_0}{\sigma_1} = \frac{B_1}{B_0}\frac{\sigma_0}{1-\sigma_0} = \frac{B_1}{B_0},$$

$$(3) \quad \frac{a_0}{a_1} = \frac{\sigma_0}{1-\sigma_0}\frac{b_0}{b_1}e^{\frac{\lambda_1-\lambda_0}{RT}} = \frac{\sigma_0}{1-\sigma_0}g\,(T).$$

If every ammonia molecule striking the surface condenses, we obtain

$$\frac{a_0}{a_1} = \frac{p_0}{p_1}\left(\frac{M_1}{M_0}\right)^{\frac{1}{2}} = \frac{\sigma_0}{1-\sigma_0}g\,(T).$$

Hence solving for σ_0 we obtain

$$\sigma_0 = \left[\frac{p_1}{p_0}\left(\frac{M_0}{M_1}\right)^{\frac{1}{2}} g\,(T) + 1\right]^{-1}.$$

At any one temperature the reaction velocity is proportional to σ_0, or

$$k = C\,(T)\left[\frac{p_1}{p_0}\left(\frac{M_0}{M_1}\right)^{\frac{1}{2}} g\,(T) + 1\right]^{-1},$$

or

$$\frac{1}{k} = \frac{g\,(T)}{C\,(T)}\left(\frac{M_0}{M_1}\right)^{\frac{1}{2}}\frac{p_1}{p_0} + \frac{1}{C\,(T)}.$$

Hence on plotting $\frac{1}{k}$ against $\frac{p_1}{p_0}\left(\frac{M_0}{M_1}\right)^{\frac{1}{2}}$ we should obtain a straight line cutting the $\frac{1}{k}$ axis at $\frac{1}{C\,(T)}$ with a slope of $\frac{g\,(T)}{C\,(T)}$.

The value of $C\,(T) = \frac{k}{\sigma_0}$ is the true rate of decomposition per unit area covered with ammonia, and $-Rd\log C\,(T)/dT^{-1}$ should be the true heat of activation Q. If $\sigma_2 = 0$ and $\sigma_0 + \sigma_1 = 1$, then

$$E = Q + (\lambda_1 - \lambda_0)(1 - \sigma_0).$$

Kunsman obtains for the decomposition of ammonia on tungsten $Q = 41{,}500$ and $\lambda_0 - \lambda_1 = 1{,}500$, on iron $Q = 41{,}600$ and $\lambda_0 - \lambda_1 = 5{,}300$ cals. per grm. mol.

Energies of activation calculated in this manner give lower values than the corresponding homogeneous reactions, and we must assume that collisions in the intrinsic field of the catalyst surface are more fruitful in reaction than those in the gas phase. Enquiries as to the reason of this lead us in two directions, firstly whether these reactive collisions occur all over the catalyst surface or only at special places, and secondly whether the increased fruitfulness or lowering of the critical energy increment is due solely to the effects of orientation which we have shown to be present, or to other reasons.

It has frequently been suggested that catalysis does not proceed at a uniform rate over the whole of an accessible catalytic surface (see Langmuir, *J.A.C.S.* XXXVIII. 2223, 1916; XL. 1361, 1918; Rideal, *J.C.S.* CXXI. 309, 1922; Second Solvay Conference, Oct 1925; Taylor, *Proc. Roy. Soc.* A, CVIII. 105, 1925; *J.P.C.* XXX. 145, 1926; Adkins, *J.A.C.S.* XLV. 811, 1923; L. 1930, 1928; LI. 2930, 1924; Cassel, *Naturwiss.* 1928; Pietsch and Schwab, *Zeit. physikal. Chem.* CXXXVII. 385, 1928). Evidence for this assumption is noted in many directions, firstly the sensitivity of a catalyst to heat treatment and the effect of minute amounts of poison on the catalytic activity. Many cases are known (cf. Vavon and Husson, *C.R.* CLXXV. 277, 1927) where the progressive addition of a poison will lower the catalytic activity apparently in stages. Supplementary evidence can be adduced by the effect of addition agents which serve as true promoters; thus copper promoted with small quantities of palladium will cause the rates of catalytic combustion of carbon monoxide hydrogen mixtures to be quite different to that anticipated from any additive law of surfaces.

It seems likely that this differentiation of the surface becomes less pronounced as the temperature is raised, for at high temperatures surfaces appear to be almost uniformly active. The views expressed concerning the structure of these active patches vary from the conception of an isolated atom forming the first member of a new lattice layer through concepts of special atomic configurations to suit each special reaction to the edges and crystal corners, including the Smekal cracks or grain boundaries.

We have already cited evidence from the oxidation of copper to the enhanced activity of surfaces in which these grain boundaries are well developed, i.e. for a surface in a microcrystalline state.

That such active boundary lines occur on catalytic surfaces indicates that orientation at the surface cannot be the sole factor responsible for the lower critical energy increment. We shall have occasion to note in discussing the adsorption of electrolytes by charcoal and by platinum that the nature and extent of the adsorption is governed by the magnitude of the interphasic potential, the solid serving as a gas electrode, and that similar observations can be made as to the mechanism of the hydrogen and oxygen electrode. The importance of the intrinsic field is also emphasised in dealing with problems of thermionic emission through thin films, and we noted that a single atom on the surface would not only be highly deformed if polarisable but would also affect its neighbours for a considerable distance around it: likewise the continued functioning of an oxide coated emitter was dependent both on lattice diffusion of ions as well as on fissure or slip plane diffusion of atoms.

It is possible that the mechanism of catalytic processes at such surfaces will be elucidated by a closer examination of the properties of and the actions caused by these intrinsic fields existing at surfaces.

CHAPTER VI

THE LIQUID-SOLID INTERFACE

1. Adsorption at solid surfaces.

We have already had occasion to note that on exposure of a fresh solid surface to a gas adsorption takes place and the surface becomes covered with a film of the gas.

On the immersion of a solid surface in a liquid the solid will be already coated with a gas film prior to immersion (unless a surface is freshly formed by condensation or by cleavage in the liquid), which must be removed before actual wetting of the solid takes place. Solids which adsorb liquids preferentially to gases are wetted after a period of immersion short or prolonged, whilst those in which the gas-solid adhesional forces are greater than those of the liquid-solid are not so wetted.

Thus glass which adsorbs the various constituents of the air more readily than it adsorbs mercury is not wetted by the metal, but if the adsorbed gas be removed from the surface, e.g. with the aid of a high vacuum such as obtains in a MacLeod gauge, the mercury may be caused to adhere to the glass.

2. Surface energy of solid-liquid interfaces.

As in the case of the solid-gas interface, it is a very difficult matter to determine the value of the surface energy of the solid-liquid interface, viz. σ_{sl}.

Attempts have been made to compute this value by the measurement of the solubility of small particles of the solid (see p. 42), notably by Ostwald (*Zeit. physikal. Chem.* XXXIV. 495, 1900), Freundlich (*Kapillarchemie*, 1920, p. 143), Hulett (*Zeit. physikal. Chem.* LXI. 385, 1901), Hulett and Allen (*J.A.C.S.* XXIV. 667, 1902), W. J. Jones (*Ann. der Phys.* IV. 441, 1913) and Jones and Partington (*J.C.S.* CVII. 1079, 1915), Dundon (*J.A.C.S.* XLV. 2479, 2658, 1925) and others.

On analogy with the surface tension effects in liquids (Ch. I) we may consider that there will be an excess pressure inside a small solid sphere immersed in a liquid equal to

$$\frac{2\sigma_{sl}}{\rho r},$$

where σ_{sl} is the interfacial surface energy, ρ the density of the solid and r the sphere radius.

The work done in transferring an amount of the material δw from a sphere of radius r_1 to one of radius r_2 will accordingly be

$$\frac{2\sigma_{sl}}{\rho}\left\{\frac{1}{r_1}-\frac{1}{r_2}\right\}\delta w.$$

If the osmotic pressures of the solutions with which the two spheres are in equilibrium be Π_1 and Π_2 respectively, the transfer of δw of the solute from one solution to another will necessitate the expenditure of energy equal to

$$\delta w\, RT \log \frac{\Pi_1}{\Pi_2} = \delta w\, RT \log \frac{c_1}{c_2}$$

for dilute solutions, i.e. for relatively insoluble salts.

Since the two systems are in equilibrium

$$\delta w\, RT \log \frac{c_1}{c_2} = \frac{2\sigma_{sl}}{\rho}\left\{\frac{1}{r_1}-\frac{1}{r_2}\right\}\delta w \quad \text{or} \quad RT \log \frac{c_1}{c_\infty} = \frac{2\sigma_{sl}}{\rho r},$$

where c_∞ is the solubility of large crystals ($r = \infty$) of the salt. Hulett found for grains of calcium sulphate, where $r = \cdot 00003$ cm., a solubility as determined by conductivity measurements $c_1 = 18\cdot 2$ millimols per litre. The normal solubility c_∞ obtaining for grains where $r > 0\cdot 0002$ cm. is 15·33 millimols per litre. From these data $\sigma_{sl} = 1100$ ergs per sq. cm.; in the case of barium sulphate σ_{sl} was found to be 1300.

The experiments of Dundon have indicated that Hulett's value for calcium sulphate is much too high, doubtless owing to the effect of grinding on the water content of the decahydrate. Dundon obtained the following values for a series of salts.

Substance	$\sigma_{s.\,water}$
PbI_2 ...	130
$CaSO_4 2H_2O$	370
Ag_2CrO_4 ...	575
PbF_2 ...	900
$SrSO_4$ ...	1400
$BaSO_4$ ...	1250 3000
CaF_2 ...	2500

There exists a rough proportionality between the surface tension and the hardness as well as an inverse proportionality to the molecular volume of the solid.

The validity of the premises on which such calculations are founded can not only be called to question by the considerations that have already been discussed concerning the solid-gas interface, but a further complication is introduced when the substance whose solubility is being determined is an electrolyte. The surfaces of the crystal adsorb not only the water in which they are suspended but also the ions of the salt in solution (see p. 280). At equilibrium there is a dynamic interchange between the ions in solution and those on the surface. In the vaporisation of an ionised salt, such as sodium chloride, the positive and negative ions evaporate as doublets except at very high temperatures when the kinetic energy of the individual ions is sufficient to rupture the electrostatic bond between the doublets. In solution however it is probable that the removal of the surface ions by reaction with the water or by solution and the re-deposition of the ions by diffusion does not necessarily occur in doublets; thus radium ions may replace barium ions at the surface of a crystal of barium sulphate immersed in a solution of a radium salt and such replacement may take place, not through the removal of a molecule of barium sulphate and substitution of the same, but by the removal of a barium ion from the space lattice and its replacement by a radium ion. In a similar manner crystals of silver chloride will adsorb silver ions onto the space lattice of the crystal—presumably where the chlorine ions are exposed. Under these circumstances the crystal will acquire an electric charge continually varying in sign, fluctuating as a positive or negative ion is in excess on the surface. The effect of this fluctuation in charge may be calculated if it be assumed that the electric charge is spread uniformly over the surface. It will then produce an expanding pressure equal to

$$\frac{\epsilon^2}{8\pi\kappa r^4},$$

where ϵ is the electric charge, κ the S.I.C. of the medium and r the radius of the crystal (McLewis, *Koll. Zeit.* v. 91, 1909; Knapp, *Trans. Farad. Soc.* May, 1921).

The effect of curvature or surface energy on the osmotic pressure and on the solubility is thus removed when

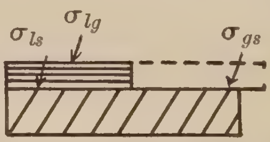
$$\frac{2\sigma_{sl}}{\rho r} = \frac{\epsilon^2}{8\pi\kappa r^4} \quad \text{or} \quad r = \sqrt[3]{\frac{\epsilon^2 \rho}{16\pi\kappa\sigma_{sl}}}.$$

In many cases an electrical double layer is formed (see Ch. VII) which enhances the difficulty of calculation.

3. The displacement of liquids at solid surfaces.

The conditions under which a liquid will wet or displace a gas in contact with a solid surface can be determined most readily by consideration of the changes in surface energy due to an increase in the area of contact between liquid and solid. If the surface energies between liquid-gas, liquid-solid, and gas-solid be denoted by σ_{lg}, σ_{ls} and σ_{gs} respectively, and a unit area of extension of the liquid over the surface of the solid is imagined to take place, we increase the surface energy liquid-solid by σ_{ls}, simultaneously increase the surface energy liquid-gas by σ_{lg} and decrease the surfce energy gas-solid by σ_{gs}. The decrease in the free surface energy is accordingly

$$\sigma_{gs} - \{\sigma_{ls} + \sigma_{lg}\}.$$



If there is a decrease in the free surface energy, the liquid will continue to displace the gas from the surface of the solid, i.e. the solid will be wetted by the liquid if

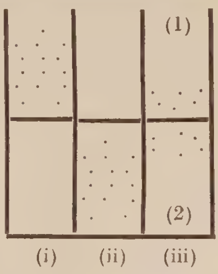
$$\sigma_{gs} > \{\sigma_{ls} + \sigma_{lg}\} \quad \text{......................(i).}$$

Similarly a second liquid (2) will displace another liquid from the surface if

$$\sigma_{1s} > \{\sigma_{2s} + \sigma_{21}\} \quad \text{......................(ii).}$$

It is clear from a consideration of equation (i) that liquids of low surface tension, i.e. small values of σ_{lg}, are more likely to wet solids than liquids of high surface tension. Thus the organic hydrocarbons of low surface tension readily wet most solid surfaces; water will wet only a limited variety of surfaces, whilst the displacement of the adsorbed air film from solids by mercury is a comparatively rare occurrence. These considerations apply to the spreading in bulk or flattening of a lens of liquid placed on a solid surface which is exposed to a gas. We must however consider the case as in the example of drops of oil of limited volume on a liquid surface (see p. 124), two-dimensional spreading of a unimolecular film across the solid surface may occur or, again, as in the case of carbon disulphide on water, molecules evaporating from the lens may condense on the solid surface and form a unimolecular film in this manner. According to Hardy (see p. 261), fatty acids on metallic surfaces spread only through the vapour phase unless the surface is already covered with a film of water when true surface spreading takes place with extreme rapidity. The spreading of solutions of acids to lenses of finite area has already been referred to, and it is difficult to believe that spreading as a unimolecular film on a dry metal surface does not take place at all, although possibly extremely slowly, for critical evidence for two-dimensional mobility was presented in the preceding chapter. We find also (equation (ii)) that oil will displace water from the surface of metallic sulphides, but that the converse takes place at the surface of powdered quartz.

Under the conditions just discussed the solid surface is rigid whilst the two liquids are brought into contact with the solid. The effect of preferential wetting of a solid surface by liquids can also be investigated by the examination of the distribution of fine solid particles placed near the interface of two immiscible liquids.



If $\sigma_{s2} > \sigma_{s1} + \sigma_{12}$, the solid particles will be preferentially wetted by the first liquid and both the second liquid and the interface will be clear and free from solid (i).

If $\sigma_{s1} > \sigma_{s2} + \sigma_{12}$, the second liquid will contain all the solid particles (ii), and finally if

$\sigma_{12} > \sigma_{s1} + \sigma_{s2}$ or if no one surface energy is greater than the sum of the two others, the particles will collect at the interface between the two liquids; the solid in this latter case increases the miscibility of the two liquids, since both liquids are adsorbed by the solid and exist in the adsorption layer as a homogeneous mixture (iii). (See p. 142, Ch. IV.)

Experiments illustrating these various possible reactions have been carried out, notably by Reinders (*Zeit. Koll. Chem.* XIII. 235, 1913) and by Hofmann (*Zeit. physikal. Chem.* LXXXIII. 385, 1913). Finely divided calcium sulphate is preferentially wetted by water in the presence of liquids, such as chloroform and benzene which are frequently termed non-polar or slightly polar. Silver iodide suspensions in water will go into the dineric interface in contact with ether, chloroform and benzene, but are removed from the water by preferential wetting in the case of butyl and amyl alcohols, whilst the reverse holds true in the case of aqueous suspensions of arsenious sulphide.

The state of aggregation of the solid occasionally affects the interfacial surface tensions sufficiently to alter the distribution between two immiscible liquids. In the case of gold, blue gold will pass to the dineric surface ether-water, whilst brown gold will remain in the aqueous phase. A protective colloid (see Ch. VIII) which affects the interfacial surface tension will also affect the distribution, since the solid-liquid interface of the original solid has been replaced by that of the protective agent liquid interface. Most protective agents for aqueous suspensions are hydrated substances, and as a result the material thus protected usually passes into the aqueous phase.

4. The heat of adsorption.

It has already been noted that in the case of the easily liquefiable vapours bulk adsorption in fissures occurs, the heat of adsorption of such a vapour at the point of saturation is evidently identical with the heat of wetting. Calorimetric determinations of the heat evolved on wetting dry solid powders with various liquids have been made, notably by Gaudechon (*C.R.* CLVII. 207, 1913), Pouillet (*Ann. Chim. Phys.* XX. 141, 1822), Junck (*Pogg. Ann.* CXXV. 292, 1865), Chappuis (*Wied. Ann.* XIX. 21, 1883), Fitzgerald (*Nature*, XLIX. 293, 316, 1894), Lagergren (*Kgl. Vetenskaps Akad.* XXIV. B, 1898). There is a wide variation in the magnitude of the heats of adsorption of a liquid, both with the nature of the adsorbing material and adsorbed liquid, as can be noted both from the data on the adsorption of vapours (see p. 230) and the following data of Gaudechon.

Liquid	Heat of adsorption in cals. per grm.		
	Adsorbing material		
	Alumina	Quartz	Sugar charcoal
H_2O ...	12·6	15·3	3·9
CH_3OH ...	11·0	15·3	11·5
$HCOOH$ ...	12·0	14·5	*ca.* 12·0
CH_3COOH	9·3	13·5	6·0
C_3H_7COOH	7·8	13·5	6·0
CCl_3H ...	9·0	8·0	2·3
C_6H_6 ...	5·8	8·1	4·2
CS_2 ...	1·7	8·6	4·0
CCl_4 ...	1·8	8·1	1·5
C_6H_{14} ...	1·2	3·1	0·4

The heat of wetting of silica and other gels with a number of liquids has been determined by Patrick and his co-workers. Patrick and Grimm (*J.A.C.S.* XLIII. 2145, 1921) obtained the following values for a silica gel.

Liquid	Heat of wetting cals. per grm.
Water	19·22
Ethyl alcohol ...	22·63
Benzene	11·13
Carbon tetrachloride	8·42
Aniline	17·52

They consider the heat liberated is due to the decrease in surface energy accompanying the immersion of the particles of the silica, which is regarded as possessing the surface energy of water.

We obtain the total surface energy per sq. cm. from the equation

$$u = \sigma - T\frac{d\sigma}{dT}.$$

Inserting the values $\sigma = 72{\cdot}05$ dynes per cm., $\frac{d\sigma}{dT} = -0{\cdot}151$ dyne per cm. per ° C., u is found to be at room temperature 117·08 ergs per cm.^{2}; this with a heat of wetting of 19·22 cals. per grm. gives a specific surface of $7 . 10^6$ cm.^{2} per grm. The total surface energy of a benzene water interface is 51·66 ergs per cm.^{2}; thus on addition of benzene 117·08 – 51·66 or 65·42 ergs per cm.^{2} are converted into heat, or 10·74 cals. per grm. of gel should be liberated, compared with an observed value of 11·13 cals. per grm. In a similar manner, calculated values of 7·10 and 16·6 cals. per grm. for wetting by carbon tetrachloride and by aniline respectively were obtained.

A more accurate investigation of the heats of wetting of known areas of solids by various liquids over an extended temperature range is highly desirable, since it offers a promising method of testing the validity of the Nernst heat theorem in connection with the thermodynamics of the surface phase. As we have already had occasion to observe, the surface tension or free surface energy is related to the total surface energy, which can be determined calorimetrically, by means of the Gibbs-Helmholtz equation $\sigma - u = T\frac{d\sigma}{dT}$. According to the Nernst heat theorem $\underset{T=0}{\mathrm{Lt}}\frac{du}{dT} = 0$ and $\underset{T=0}{\mathrm{Lt}}\frac{d\sigma}{dT} = 0$. The thermal changes should on analogy with Debye's investigations on the energy content of substances at low temperatures be expressible in the form $u = u_0 - aT^4$, where a is determinable from the heat capacity of the surface film, and the temperature coefficient of the heat of wetting should decrease rapidly as we approach the absolute zero. Furthermore, it is evident that at this temperature the free and total surface energies should be identical in value, the total surface energy sinking first slowly and then rapidly as the critical temperature is reached. Confirmation likewise of the assumption $\underset{T=0}{\mathrm{Lt}}\frac{d\sigma}{dT} = 0$ or that the temperature coefficient of the free surface energy should fall as we approach the absolute zero is lacking, but the relationship does not appear to hold for the gases nitrogen, argon and hydrogen over the temperature range already investigated. In addition the relationship between the free and total surface energies which should obtain at low temperatures, viz. $\sigma = u_0 + \frac{aT^4}{3}$, is markedly different to that obtained at high temperatures (see p. 33).

Very few attempts have been made to estimate the heat of adsorption per sq. cm. owing to the difficulty in computing the area.

Parks (*Phil. Mag.* VI. 4, 247, 1902) has estimated the heat of adsorption of water on silica at 7° C. as 0·001005 calorie per sq. cm. Gaudechon's quartz would thus expose a surface of 1450 sq. metres per grm., whilst Koehler and Matthews (*J.A.C.S.* XLVI. 1166, 1924) obtained a value of somewhat less than $1{\cdot}69 . 10^{-6}$ cals. per sq. cm. for dry lead sulphate.

5. Adsorption in lubrication.

The effect of adsorption of a number of substances on the coefficient of friction between solid surfaces has been the subject of detailed enquiry by Sir W. B. Hardy (*Proc. Roy. Soc.* A, C. 550, 1921; CI. 487, 1921; CIV. 25, 1923; CVIII. 1, 1925; CXII. 63, 1926). Definite evidence is presented that at metallic surfaces polar groups are strongly adsorbed. On placing a load on a lubricated surface the load floats on the multimolecular layer which can be squeezed out by increasing the load until presumably a bimolecular layer with the molecules orientated towards the metal and load interface is left. The friction gradually rises as the multimolecular layer is squeezed out until it acquires a constant value dependent on the chemical constitution of the lubricant, as is shown by the following data for bayonne oil.

Time	μ	Time	μ
5 secs.	0·02 approx.	120 mins.	0·323 approx.
1 min.	0·11	210 ,,	0·335
5 mins.	0·20	270 ,,	0·336
15 ,,	0·282	8 hrs.	0·338
45 ,,	0·296		

For the limiting layer of lubricant the coefficient of friction is found to be a linear function of the molecular weight of a homologous series and may be expressed in the form

$$\mu = b_0 - d - c\,(N - 2),$$

where b_0 is the friction of the clean faces, i.e. a function of the chemical nature of the solid, d is the decrement in friction due to the polar groups and c the decrement in friction due to each carbon atom in the chain of length N. When the polar end is a carboxyl group the friction actually vanishes when N exceeds fifteen, the smallest traction that can be applied producing slip.

The temperature coefficient of static friction has been investigated by Hardy and Doubleday (*Proc. Roy. Soc.* A, CI. 489, 1921), a slider having a spherical face being made to slide over the plate in an atmosphere of clean dry air.

It was found that over the range 15–110° C. steel, bismuth and quartz when clean and dry showed no changes in the values for the static frictions, and when these surfaces were lubricated with lubricants which were fluid over this temperature range likewise no changes were observed. Some of the values obtained are shown in the following table.

Lubricant	Steel μ	Quartz μ
None	—	0·770
Undecane ...	0·34	0·49
Caprylic acid ...	0·20	0·306
Pelargonic acid	0·14	0·238
Butyl alcohol	0·39	0·545
Octyl ,,	0·29	0·457
Undecyl ,,	0·23	0·39

With lubricants which were solid at low temperatures and melted between 15° C. and 110° C., the friction was found to fall. At the melting point the friction suddenly falls to zero and when fully melted the constant value for the coefficient of friction of the liquid lubricant suddenly appears.

On cooling from 110° C. this point of discontinuity at the melting point is again observed, a sudden fall in μ occurs, but not to zero as with the ascending temperatures. The discontinuity at the melting point was found to be due to the fact that when the lubricant was solid the friction measured was that of the lubricant itself, for on eliminating this factor by depositing thin films of the lubricants from ethereal solutions on the solid faces constant values for the static frictions were obtained over the whole temperature range 15–110° C. The following are typical of the values obtained.

Lubricant	Steel μ	Quartz μ
$C_{19}H_{40}$ ...	0·179	0·324
$C_{22}H_{46}$ ...	0·110	0·26
$C_{24}H_{50}$ ...	0·068	0·23
Cetyl alcohol	0·114	0·276
Decoic acid ...	0·075	0·18
Undecoic acid	negligible	0·114
Palmitic acid	negligible	negligible

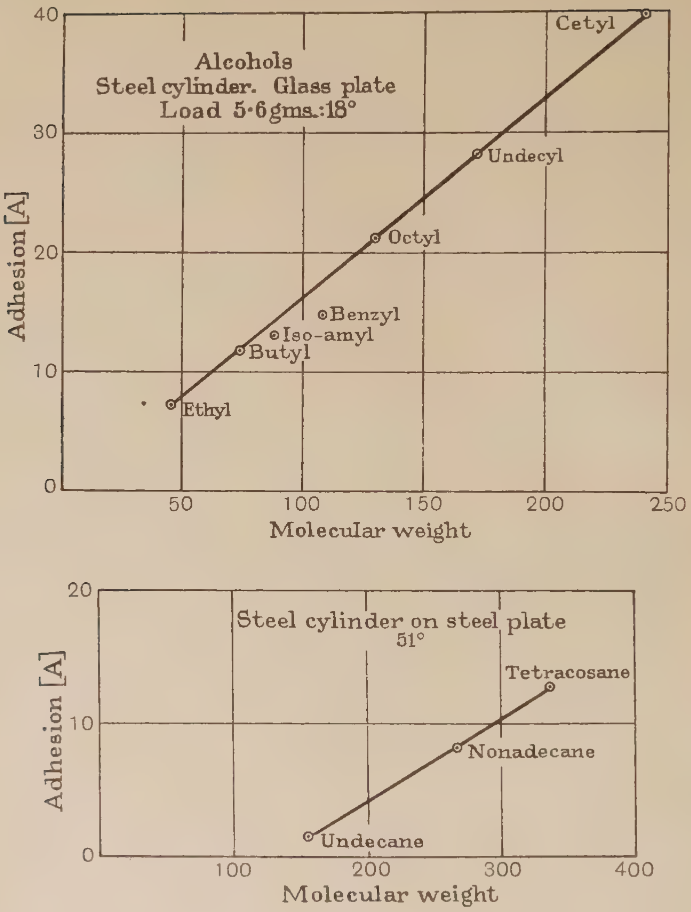
We may note that if the heat of wetting of these surfaces be *ca.* 5000 cals. per grm. mol, the alteration in molecular density calculated by the Boltzmann equation of the wetting film will be only from $e^{8\cdot 6}$ to e^7; an extension of these observations to still higher temperatures would thus appear to be eminently desirable.

Whilst friction is measured by the tangential reaction at the interface to external forces, the normal reaction may be termed adhesion; this has likewise been examined by Hardy. As in the case of the tangential reaction, there exists a latent period which however was not observed with octane and cyclohexane but only with substances with polar groups. This observation lends support to the hypothesis that a relatively long time is necessary for the orientation of the molecules both in the primary and also in the outer layers to attain equilibrium conditions.

Measurements of the adhesion were accomplished by determining the force required to detach a cylinder with different loads instantaneously from a plate flooded with the lubricant. A few of these are given in the table below for 18° C.

Liquid	Load grms.	Adhesion A steel glass grms.	Adhesion A steel steel grms.
Octane ...	5·6	1·2	1·1
	115·1	3·0	2·8
	259·6	3·8	3·3
Ethyl alcohol	5·6	7·2	5·2
	115·1	22·1	14·2
	259·6	33·9	23·2
Heptylic acid	5·6	12·7	—
	115·1	50·9	—
	255·6	54·9	—

The value of the adhesion was found to depend not only on the chemical nature of the lubricant but also on the solids, those examined always giving the order glass > steel > copper. The values for the adhesions of alcohols and hydrocarbons are given in the graphs on p. 264.



Adsorption from Solutions.

6. Non-electrolytes.

If an aqueous solution of some colouring matter be agitated with powdered charcoal and a determination of the concentration of the colouring matter in the solution be made both before and after the operation, the solution will be found to be much less concentrated. Such selective removal is frequently termed positive adsorption.

As a rule the solutes which are positively adsorbed by solid adsorbents are negatively adsorbed at a gas-liquid interface. Such behaviour is in agreement with Antonow's rule that

$$\sigma_{a\,\mathrm{vapour}} = \sigma_{b\,\mathrm{vapour}} + \sigma_{ab},$$

where a and b are two phases in equilibrium (in his limited definition two mutually saturated liquids) of which a has the higher surface tension against vapour.

Now Antonow's rule appears to be valid for two liquids provided that "saturation" be carefully defined, and it is true for solid and liquid interfaces provided that the angle of contact be zero. Thus

$$\sigma_{\mathrm{charcoal,\ water}} = \sigma_{c\ \mathrm{air}} \sim \sigma_{\mathrm{H_2O\ air}} \quad \cdots\cdots\cdots\cdots\cdots\text{(i)},$$

$$\sigma_{\mathrm{charcoal,\ KCl\ solution}} = \sigma_{c\ \mathrm{air}} \sim \sigma_{\mathrm{KCl\ aq.\ air}} \quad \cdots\cdots\cdots\text{(ii)}.$$

Now $\sigma_{c\ \mathrm{air}} > \sigma_{\mathrm{H_2O\ air}}$ or $\sigma_{\mathrm{KCl\ aq.\ air}}$, otherwise charcoal would not adsorb water, so we may replace ~ above by −.

From (i) and (ii) we obtain

$$\sigma_{c\mathrm{H_2O\ air}} - \sigma_{c\mathrm{KCl\ aq.\ air}} = \sigma_{\mathrm{KCl\ aq.\ air}} - \sigma_{\mathrm{H_2O\ air}} > 0,$$

so that whilst potassium chloride raises the surface tension of water-air it lowers the surface tension water-charcoal and is therefore positively adsorbed at the interface.

It must however be pointed out that in the above deduction we have assumed

$\sigma_{\mathrm{charcoal,\ water}}$ is equivalent to $\sigma_{\mathrm{charcoal\ saturated\ with\ water,\ water}}$

as demanded by Antonow's rule. There is probably a not inconsiderable difference between these values (cf. mercury saturated with organic vapours, p. 76). This difference may be used as a possible explanation of why some solutes in water are positively adsorbed both at an air and a charcoal interface.

This property of selective removal is utilised largely in industry, and the following table from Bancroft indicates the values of some of the more important decolourising agents.

Material	Efficiency	Material	Efficiency
Alumina ...	100	Fuller's earth II	17
Fuller's earth I ...	50	Ferric oxide ...	17
Bauxite... ...	50–30	Ball clay ...	14
Ignited peat ...	25	Fuller's earth III	10
Bone charcoal ...	24	China clay ...	3
Bog iron ore ...	20	Kieselguhr ...	3

The rate and completeness of removal is generally greater at high temperatures and is in general proportional to the fineness of the mesh; bauxite, for example, increases its efficiency from 100 for a 40/80 mesh to 170 for a 60/80 mesh.

The property of adsorption from solutions of a particular solute is in general, apart from the fact that both solvent and solute are adsorbed (see p. 268), complicated by the fact that the adsorbing surface presented to the liquid is not uniform but broken up into a series of fissures or capillaries as is the case with solids such as charcoal and pumice or "gels" such as those of silica and alumina, with the result that true equilibrium between solution and adsorbent may not result until after long periods of time, necessary for the intradiffusion of the solution into the absorbent, during which period secondary chemical action may take place. For comparative purposes adsorption as distinguished from absorption or sorption (J. W. McBain, *Phil. Mag.* XVIII. 6, 1909) is considered to take place rapidly in solutions as well as in gases (see p. 168).

The early experimental data of Freundlich (*Kapillarchemie*) indicated that the adsorption of a solute from a solution followed the general laws governing the adsorption of vapours by solids, i.e. the Freundlich isotherm

$$x = Kc^{\frac{1}{n}} \quad \text{or} \quad x^n = Kc.$$

The values of the exponent n are found to vary in the most diverse manner, as is exemplified by the following:

Adsorbent	Solute	Solvent	n
[*]Silica	KCl	H_2O	1
[†]SnO_2	"	"	1
[‡]Charcoal	"	"	1
[§]Cr_2O_3	Alizarine	"	3
[‖]Cellulose	Methylene blue	"	2
[‖]Silk	Indigo carmine	"	2
Basic lanthanum acetate	I_2	"	2
[¶]Starch	"	"	5

[*] Schmidt, *Zeit. physikal. Chem.* XV. 56, 1894.

[†] Van Bemmeln, *Zeit. anorg. Chem.* XXIII. 113, 1900.

[‡] Lachs and Michaelis, *Zeit. anorg. Chem.* XVII. 2, 1911.

[§] Georgievics, *Zeit. Farbenindustrie*, II. 253, 1903.

[‖] Biltz, *Ber.* XXXVII. 719, 1904.

[¶] Küster, *Liebig Ann.* CCLXXXIII. 364, 1871.

In general however the values of the exponent n are not whole numbers but fractional, as in the following cases:

Adsorbent	Solute	Solvent	n
Silk	Picric acid	H_2O	2·88*
		C_2H_5OH	2·75*
Charcoal	Acetic acid	H_2O	2·35†
		C_6H_6	2·40†

* Appleyard and Walker, *J.C.S.* LXIX. 1334, 1896.
† Freundlich, *Kapillarchemie.*

7. Adsorption of solvent and solute.

The adsorption of a particular solute from a solution is however dependent upon the nature of the solvent, a point not envisaged by the Freundlich isotherm. The influence of the solvent on the amount of adsorption of a particular solute has been investigated in the case of iodine and charcoal by Davis (*J.C.S.* XCI. 1666, 1911), who found that the amount of iodine adsorbed by charcoal from solutions of equimolecular concentrations decreased with the nature of the solvent in the following order:

Blood charcoal ... CCl_3H, C_2H_5OH, $CH_3COOC_2H_5$, C_6H_6, $C_6H_5CH_3$,
Sugar charcoal ... CCl_3H, $C_6H_5CH_3$, $CH_3COOC_2H_5$, C_6H_6, C_2H_5OH.

Although in part this order may be affected by subsequent reaction of the iodine with the organic solvent under the influence of catalytic material in the charcoal (Schmidt, *Ziet. Kolloid. Chem.* XIV. 242, 1914), yet similar alterations have been noted by Freundlich (*ibid.* p. 260) with other solutes, e.g. benzoic and picric acids, who found the following order for decreasing adsorption for benzoic acid: water, benzene, ethyl, ether, acetone; for picric acid: water, ethyl, alcohol, benzene.

That the solvent plays an important part in the adsorption process is evident from the various cases of "negative" adsorption (Gore, *Chem. News*, LXIX. 23, 1894; Lagergren, *Bihang till k. Svenska Vet. Akad. Hand.* II. 244; Trouton, *B.A. Reports*, 328, 1911; Gustafson, *Zeit. physikal. Chem.* XCI. 385, 1916) in which a solution shaken up with the adsorbing agent has apparently increased in concentration instead of decreasing as would be anticipated.

Williams (*Trans. Farad. Soc.* x. 1914) has shown that on the assumption that both solvent and solute are adsorbed by the adsorbing agent we may obtain "positive," "zero" or "negative" adsorption as the solute is adsorbed more strongly, equally or less strongly than the solvent and that as an alteration in concentration of the solution takes place the adsorption may pass through all these separate phases.

If we denote by u and w the amount in grams of solute and solvent adsorbed per gram adsorbent when in equilibrium with a solution containing c grams of solute per gram of solute, we find that the excess of solute per gram adsorbent, generally called the amount adsorbed u_0, is given by

$$u_0 = u - w\frac{c}{1-c}.$$

If in dilute solution when c is small the true adsorption u is proportional to concentration or $u = kc$, we obtain

$$u_0 = u - wc = (k - w)\,c,$$

or

$$u_0 = k'c,$$

where k' may be either positive or negative. Whilst in concentrated solution where c is nearly unity we have a relationship of a similar type

$$w = k'\,(1-c),$$

or

$$w_0 = (k' - v)\,(1-c),$$

or

$$u_0 = u - \frac{w}{1-c} = u - k'.$$

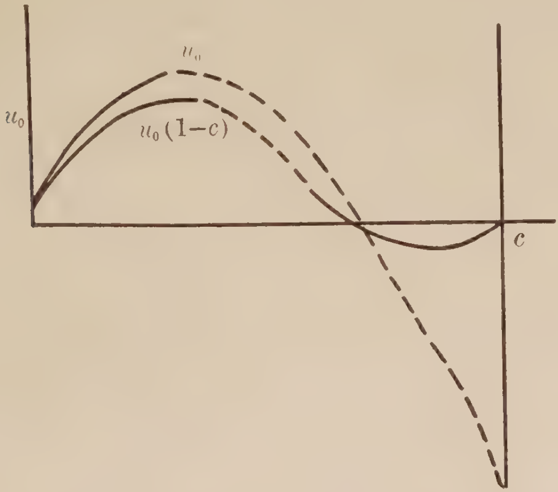
If w_0 is positive near $c = 1$ as u_0 is generally positive near $c = 0$, it follows that near $c = 1$ u_0 will be negative; hence the c, u_0 and c, $u_0\,(1-c)$ curves will be of the type shown on p. 269.

Or, in general, positive adsorption rising to a maximum will be followed by zero and eventually negative adsorption, due to the fact that solvent and solute are both adsorbed.

In a few cases examined Williams has actually obtained this transition as instanced by the following data for the adsorption of potassium chloride in aqueous solution by charcoal.

c	u_0
·00044	+ ·00032
·00616	+ ·00230
·02050	+ ·00250
·05630	+ ·00170
·06800	− ·00170
·12800	− ·00260
·17000	− ·00770

Similar results were obtained with magnesium sulphate, whilst with ammonium chloride a maximum was found; this was not followed by negative adsorption over the concentration range examined.



Osaka (*Mem. Coll. Sci. Kyoto Univ.* I. 257, 1915) has obtained positive adsorption in the case of sodium and potassium nitrates and for potassium bromide and iodide, and negative adsorption in the case of sodium and potassium sulphate as well as potassium iodide.

Gustafson (*Zeit. physikal. Chem.* XCI. 405, 1916) has attempted to extend the conception of Williams that solvent and solute are both adsorbed with the aid of the Freundlich isotherm in the following way.

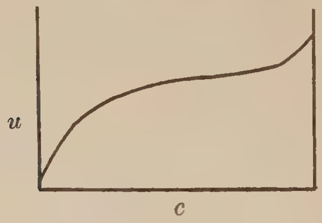
In general there will be u grams of solute and w grams of solvent adsorbed per gram of adsorbing agent. If u_∞ and w_∞ be the respective amounts adsorbed in pure solvent and solute respectively, Gustafson finds in the case of aqueous acetic acid and charcoal that

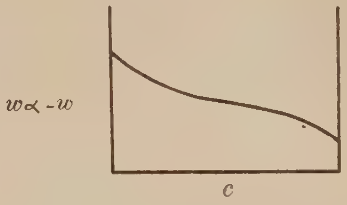
$$u = kc^{\frac{1}{n}}$$

and

$$w_\infty - w = k'c^{\frac{1}{n'}},$$

and the dual adsorption can be represented by two curves.





Williams (*Meddel. från vet. Akad. Nobelinstitut*, II. 27, 1913) on the other hand has found that a more general relationship of the type

$$\frac{u}{u_\infty} + \frac{w}{w_\infty} = 1$$

gives a fair approximation to the experimental data.

The direct determination of the amount of solvent adsorbed by an adsorbing agent is a matter of some difficulty. The most general method suggested by Arrhenius (see Williams, *loc. cit.*; Osaka, *Mem. Coll. Sci. Kyoto Univ.*, I. 257, 1915) is to leave the dry adsorbent in a desiccator exposed to the vapour of the pure solvent or solution containing a non-volatile solute. The method is open to two serious defects. As instanced by the experiments of Davis, the adsorption of a solute is affected by the simultaneous adsorption of the solvent. Thus there is no justification for the assumption that the amount of, say, water adsorbed by charcoal exposed to water vapour above a certain concentrated solution of sodium chloride will be identical with the amount of water adsorbed by the charcoal if immersed in that solution. Again, if sufficient length of time be given for the exposed charcoal to attain equilibrium with the vapour, the water vapour will enter the pores and capillaries of the charcoal and condense, thus yielding too high values for the adsorbed water. Bakr and King (*J.C.S.* CXIX. 456, 1921) have attempted to obviate these difficulties in the case where both solvent and solute are volatile by maintaining the adsorbing agent at a higher temperature than the liquid with which it is desired to attain equilibrium. A fair agreement was obtained between the amounts adsorbed by charcoal by distilling benzene from the liquid to the charcoal on the one hand and by the reverse process vaporising the excess benzene from a moist charcoal to the liquid. A knowledge of the composition of the adsorbed two-dimensional phase which is in equilibrium with a three-dimensional phase, the liquid of known composition, would together with information on the molecular diameters of the constituents in the adsorbed phase give us a direct method for evaluating the specific surface of the adsorbing material.

An extensive series of measurements of the adsorption of vapours from binary mixtures by charcoal has been carried out by Tryhorn and Wyatt (*Trans. Farad. Soc.* XXI. 399, 1925; XXII. 134, 139, 1926; XXIV. 36, 1928). From a knowledge of the total weight of vapour adsorbed by charcoal and the composition and quantity of the mixed liquids below the charcoal the quantities of each substance adsorbed are readily determined. It was found that in general the progress of adsorption from the binary saturated vapour phase underwent three stages, a first stage in which the ratio of adsorption of the two components followed closely the composition of the vapour phase, a second stage in which the composition of the "adsorbed" phase gradually changes until its composition is such as to be in equilibrium with the liquid phase, and a final stage in which isothermal distillation of the bulk liquid into the intergranular spaces of the charcoal occurs. They have examined the systems alcohol-benzene, alcohol-acetone, acetone-benzene; a few data typical of their results are summarised overleaf.

Bartlett and Sloan (*J.A.C.S.* LI. 1637, 1643, 1929) have examined the change in composition of binary liquids on the addition of active charcoal by interferometric methods, and conclude that the change in concentration as a result of adsorption can be expressed as a result of the difference between two

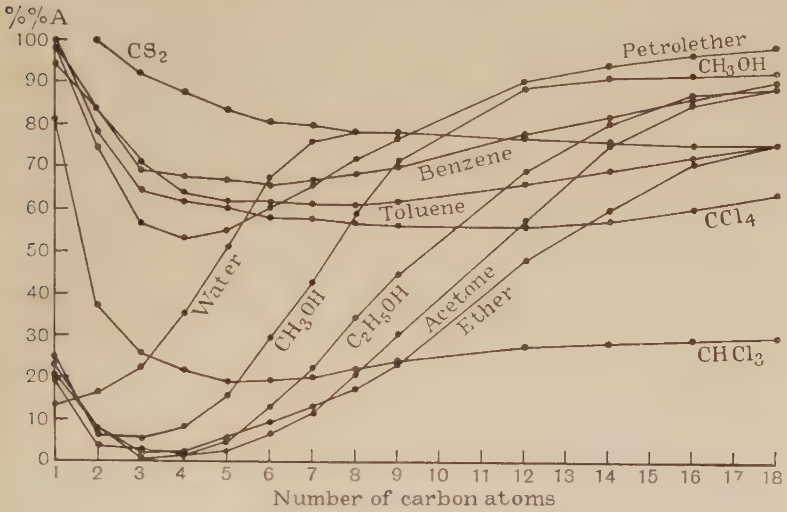
Acetone benzene				Ethyl alcohol-benzene		
Equilibrium mixture Mols % acetone		Adsorbed phase		Equilibrium mixture Mols % alcohol		
Liquid	Vapour	Acetone grm. mols × 10^5	% alcohol	Liquid	Vapour	Adsorbed phase % acetone
6·7	20·1	46·0	24·8	7·9	19·9	29·1
17·0	36·0	85·5	44·3	17·5	26·8	30·2
30·5	50·8	118·0	59·0	29·0	29·9	33·0
45·4	64·4	143·5	68·5	41·1	31·3	33·65
61·2	75·0	168·0	79·2	56·2	34·5	36·3
75·2	84·6	189·0	86·0	72·6	42·0	41·3
93·8	94·8	217·0	96·5	85·2	53·2	50·9
100·0	100·0	226·0	100·0	97·9	87·0	83·9

Freundlich isotherms, one applicable to each constituent; thus for ethyl alcohol and benzene the decrease in concentration of benzene due to adsorption both from dilute and concentrated solutions of benzene in ethyl alcohol may be represented by the expression $k = 9{\cdot}76c^{0{\cdot}532}(1-c) - 6{\cdot}26(1-c)^{0{\cdot}662}$, where c is the molar fraction of benzene. The agreement is shown in the following table.

c	k	Observed
0·00513	0·555	0·521
0·01050	0·790	0·787
0·1033	2·014	2·022
0·1725	2·220	2·213
0·3907	1·847	1·672
0·7630	0·163	0·164
0·8706	– 0·232	– 0·203
0·9194	– 0·341	– 0·412
0·9641	– 0·323	– 0·337
0·9870	– 0·256	– 0·255

It will be noted that the data yield an S-shaped curve as obtained by Williams.

The adsorption of a homologous series of aliphatic straight-chain fatty acids from various solvents by charcoal and from a few solvents by stearic acid has been examined by Vekrassow (*Zeit. physikal. Chem.* CXXXVI. 25, 1928); the results of the investigation for charcoal are summarised in the following diagram.



The partition of these substances containing a polar head and a non-polar chain between solvent and surface will depend on the magnitudes of the relative adhesions of both chain and head for the two phases. It will be observed that both the polar head and the chain possess a marked adhesion for charcoal, for in a non-polar solvent the short chain acids are more strongly adsorbed, whilst in polar solvents the long chain acids adhere more strongly.

8. The adsorption of electrolytes by charcoal.

With ordinary charcoal as adsorbing agent Michaelis and his co-workers (Lachs, *Koll. Zeit.* IX. 275, 1911; Rona, *Biochem. Zeit.* XCIV. 240, 1919; XCVII. 85, 103, 1920; Hartleben, *Biochem. Zeit.* CXV. 46, 1921) found that on adsorption of a series of salts possessing common anions or cations the adsorption is an additive property of the cation and anion. Thus the order of adsorption of a series of sodium salts of various acids is identical with the order for the potassium or ammonium salts. The following series in decreasing adsorptive power was found.

CATIONS.

Organic colour bases
$> H^{\cdot} > Ag^{\cdot} > Hg^{\cdot\cdot} > Cu^{\cdot\cdot} > Al^{\cdot\cdot\cdot} > Zn^{\cdot\cdot} > Mg^{\cdot\cdot} > Ca^{\cdot\cdot} > NH_4^{\cdot} > K^{\cdot} > Na^{\cdot}$

ANIONS.

Organic colour acids
$> OH' > CN' > S'' > I' > NO_3' > Br' > Cl' > HPO_4'' > SO_4''$

(See also Morawitz, *Koll. Chem. Beihefte*, I. 301, 1910.)

In all cases comparisons were made with dilutions electrically equivalent, e.g. $0{\cdot}1N$ NaCl, $0{\cdot}05N$ $MgCl_2$, $0{\cdot}033N$ $AlCl_3$.

In the case of an acid such as hydrochloric acid the hydrogen ions were found to be more readily adsorbed than the chlorine ions; expressed in terms of the Freundlich isotherm we obtain two independent equations

$$x_{\dot{H}} = a\,[\dot{H}]^{\frac{1}{n}},$$

$$x_{Cl'} = a'\,[Cl']^{\frac{1}{m}}$$

where in general $a \neq a'$ and $\frac{1}{n} \neq \frac{1}{m}$.

The selective adsorption of the hydrogen ions cannot proceed to true equilibrium owing to the electrostatic attraction between the dissimilar ions; consequently chlorine ions are adsorbed in excess of their equilibrium concentration and, since the hydrogen ions on adsorption have to do work in increasing the surface concentration of chlorine ions above their proper value, the true adsorption value of the hydrogen ions is not attained.

On the addition of a neutral chloride to the solution the chlorine ion concentration is increased, and provided that the cation of the added chloride does not affect the adsorption of the hydrogen ion, i.e. on addition of a weakly adsorbed cation, such as potassium, the adsorption of the hydrogen ion can now proceed to its normal equilibrium value without having to retain any adsorbed chlorine ions by electrostatic attraction. The addition of potassium chloride to a hydrochloric acid solution will thus augment the adsorption of the acid by the charcoal, a result confirmed by Michaelis and Rona.

Identical maximal values for the adsorption by blood charcoal were found for the acids HCl, HNO_3, H_2SO_4 in the presence of their neutral salts, viz. a 45 % adsorption in a $0{\cdot}01$ molar solution. Similar results were obtained for the adsorption of hydroxyl ions, e.g. caustic potash and soda, in the presence of excess potassium and sodium chlorides, both hydrogen and hydroxyl ions exhibiting equal adsorption.

Different results however are obtained when pure charcoal, i.e. ashless and activated at high temperatures, is employed. Such charcoal has been employed by several investigators, notably Bartell and Miller (*J.A.C.S.* XLIV. 1866, 1922; XLV. 1106, 1923), Miller (*ibid.* XLVI. 1150, 1924; XLVII. 1270, 1925; *J.P.C.* XXX. 1031, 1062, 1926; XXXI. 1197, 1927; *Coll. Symp. Mon.* V. 55, 1928; *J.P.C.* XXXII. 829, 1928), Ogawa (*Biochem. Zeit.* CI. 275, 1915; CLXXII. 279, 1926), Schilow (*Zeit. physikal. Chem.* CXXXIII. 188, 1928), Dubinin (*ibid.* CXXXV. 29, 1928) and Kolthoff (*Rec. Trav. Chim. Pays-Bas,* XLVI. 549, 1927).

Such charcoals immersed in ordinary solutions containing dissolved oxygen readily adsorb acids, but do not adsorb strong inorganic bases. The adsorption for acids is so marked that salts such as sodium chloride undergo hydrolytic adsorption, the solution becoming alkaline.

Frumkin and his co-workers (*Zeit. anorg. Chem.* CLVIII. 84, 1926; *Ber.* LX. 1816, 1927; *Zeit. physikal. Chem.* CXLI. 3, 1929) have drawn attention to the fact that since charcoal in aqueous solutions can serve as a gas electrode, either as a hydrogen or hydroxyl electrode, the amount and nature of the adsorption of an electrolyte in the solution will be dependent on the potential difference between charcoal and solution. An active charcoal containing a small amount of platinum and agitated with a salt solution in a hydrogen atmosphere sends hydrogen ions into solution and thus adsorbs alkali hydrolytically instead of acid rendering the solution acid.

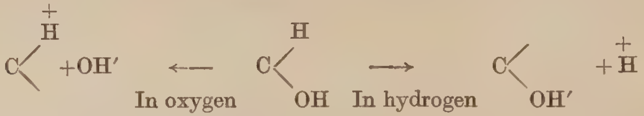
In oxygen containing solutions OH' ions are sent into solution, the charcoal acquires a positive charge and anions are adsorbed resulting in a basic solution.

The marked differences obtained are shown in the data given overleaf for 0·25 grms. of charcoal agitated with 10 c.c. of 0·0107N HCl and 0·059N NaOH respectively.

It will be noted that less than 0·2 % of platinum is sufficient to render the charcoal electromotively active so that it can

% Pt	HCl adsorbed in		NaOH adsorbed in		Acid	Normality	Adsorbed on 0·2 % Pt charcoal in	
	air	H_2	air	H_2			air	H_2
0·0	0·227	0·190	0·00	0·00	HCl	0·01	0·307	0·00
0·004	0·298	0·116	0·00	0·00	H_2SO_4	0·01	0·316	0·00
0·16	0·358	0·000	0·00	0·521	H_3PO_4	0·01	0·366	0·00
0·8	0·376	0·000	0·00	0·557				
4·0	0·393	0·000	0·00	0·576				
10·0	0·406	0·000	0·00	0·582				

function as a perfectly reversible electrode of the type



coming rapidly into equilibrium in the solution. In the absence of the platinum, adsorbed oxygen (Ch. v) is not readily removed from the surface; thus this case presents a typical example of promoter action.

We may note that at the isoelectric point of the charcoal the adsorption of any non-electrolyte will be at a maximum; thus Wright and Rideal (*Trans. Farad. Soc.* XXIV. 530, 1928) obtained the maximum rates of decomposition of solutions of hydrogen-peroxide at various surfaces, including charcoal, at their respective isoelectric points obtained by adjusting the P_H of the solutions.

Platinum black behaves in a manner analogous to carbon in that its adsorbing power for electrolytes is governed by its behaviour as a gas electrode; both Frumkin and Donde (*Ber.* LX. 1816, 1927) and Kolthoff and Kameda (*J.A.C.S.* LI. 2888, 1929) have shown that in an atmosphere of hydrogen alkali is hydrolytically adsorbed from a salt solution; hydrochloric acid is adsorbed in the presence of oxygen but not in a hydrogen atmosphere. Caustic soda is strongly adsorbed in a hydrogen atmosphere, the adsorption maximum occurring at ·0007N. In oxygen caustic soda is also adsorbed, but this exception is found to be due to the neutralisation of the hexaquoplatinic acid $Pt(OH)_6$ present in the platinum black.

In the case of weak acids, such as the organic acids, the extent of adsorption when no special precautions are taken to ensure the absence of dissolved gases is greatly dependent on the acidity of the solution; thus Phelps and Peters (*Proc. Roy. Soc.* A, CXXIV. 584, 1929) and Phelps (*J.C.S.* CCXXVII. 1724, 1929) have found that in the presence of buffers the adsorption of these acids is roughly proportional to the amount of non-ionised acid present as calculated from the dissociation constants. We may note that in these feebly acid solutions hydroxyl ions will be sent into solution to an extent dependent on the acidity of the solution; the charcoal thus acquires a positive charge and organic anions will be adsorbed; this adsorption will, to a first approximation, be proportional to the hydrogen ion concentration and to the anion concentration of the solution, which by the ordinary mass law is proportional to the concentration of undissociated molecules. Thus these experiments might well be repeated in gas free solutions so as to distinguish between the two possible modes of adsorption.

Examination of the adsorption from aqueous solutions by silica has led to anomalous results. Bartell and Fu (*J.P.C.* XXXIII. 676, 1929) obtained regular Freundlich adsorption isotherms for the bases $LiOH > NaOH > KOH > NH_2OH$, but failed to observe adsorption of strong inorganic acids; the organic acids are however adsorbed, the adsorption decreasing as we proceed up the homologous series. Silica was likewise found to adsorb bases from salts hydrolytically.

9. Adsorption of electrolytes by heteropolar surfaces.

The formation of mixed crystals, one of the criteria for isomorphism, reveals the fact that similarity of crystal lattice between two salts in the solid state coincides with a marked mutual adsorption of the respective ion pairs from solutions, e.g. the marked adsorption of sodium nitrate by homo-omorphous calcite and potassium nitrate by aragonite (Marc, *Zeit. physikal. Chem.* LXXV. 710, 1911; LXXXI. 641, 1913). In the more general cases of a crystal immersed in an electrolyte we note that if the electrolyte contains an ion common to that forming the crystal and thus fitting into the lattice, that ion will be most strongly adsorbed, giving rise to electrokinetic potentials to be discussed later. The selective adsorption of silver ions from silver nitrate and of iodide ions from potassium iodide by silver iodide, resulting in positively and negatively charged suspensions, may be cited as an example of the strong adsorption of a common ion. The extent to which the other ion of the electrolyte is likewise adsorbed as well as the extent of adsorption of non-isomorphous salts possessing no ion common with the adsorbing crystalline surfaces have been examined especially by Paneth (*Phys. Zeit.* XV. 924, 1914; *Zeit. physikal. Chem.* LXXXIX. 513, 1915), Fajans (*ibid.* XCVII. 480, 1921), Weiser and Sherrick (*J.P.C.* XXIII. 205, 1919), Dhar and Ghosh (*Koll. Zeit.* XXXV. 144, 1924), Mokrouchine (*J. P. Ch. Russ.* LVIII. 737, 1926), Pinkus and Brouckére (*J. Chem. Phys.* XXV. 606, 1928; XXVI. 251, 1929). Paneth pointed out that not only were common ions readily adsorbed but likewise those ions which formed relatively insoluble salts with the oppositely charged ion in the crystal lattice; thus whilst the barium ion is strongly adsorbed by barium sulphate, so also are lead ions. Lead ions will likewise be adsorbed by silver halides owing to the sparing solubilities of the lead halides.

Fajans investigated the adsorption of lead and its isotopic thorium B by the silver halides. In the presence of excess silver ions in solution produced by the addition of excess of silver nitrate there is practically no adsorption of thorium B, but in presence of excess halide marked adsorption occurred. Some of the data are shown below.

AgBr	Excess Br′ millimol/litre	Increase % adsorption ThB
0·4	7·2	6
1·2	3·6	20
1·6	4·8	13
2·0	4·0	17
3·8	0·4	6
20·0	40·0	85

The adsorption of an insoluble salt-forming cation is thus greatly enhanced by the covering up of the cations in the surface of the crystal lattice by addition of the common anion to the solution.

Pinkus and Brouckére, treating the ionic adsorption as a dynamic process in a manner similar to that developed by Langmuir (p. 194), develop the expression for the amount adsorbed in terms of the activity of the electrolyte in the solution

$$x = \frac{fc}{A + Bfc}.$$

In this expression the alteration in adsorption due to the electric charges of the ions already adsorbed is neglected; they assume that this will be a function of the amount adsorbed of the form

$$fx = ax^n$$

and that the charges on the crystal surface will modify the rate of resolution included in the term A in the above expression, giving

$$x = \frac{fc}{Ax^n + Bfc}.$$

The adsorption isotherms of several monovalent and divalent chlorides by barium sulphate from aqueous solution were determined and found to agree well with the above expression. The data are summarised in the following table.

Salt	$A \times 10^{-3}$	n	$B \times 10^{-3}$
HCl	1·771	0·0825	0·2239
LiCl	1·362	0·0642	2·975
NaCl	0·771	0·0258	4·891
KCl	1·563	0·0700	6·650

We may note that the adsorption of a non-electrolyte by a heteropolar surface will be at a maximum at the isoelectric point; thus Frumkin and Obrutschewa (*Biochem. Zeit.* CLXXXII. 220, 1927) observed this maximum for the adsorption of various capillary active substances from aqueous solutions by silver iodide, the adsorption becoming much less as potassium iodide or silver nitrate containing the respective readily adsorbable common ions is added to the suspension.

In addition the lateral conductivity of the film of liquid in contact with the solid should exceed that of the bulk solution due to the enrichment of the ions in the double layer. Stock (*Anzeig. Akad. Wiss. Krakow*, A, 635, 1912; 131, 1913; 95, 1914), Laing and McBain (*J.C.S.* CXVII. 1506, 1920), Fairbrother (*ibid.* CXXV. 2319, 1924; CXXV. 2495, 1924), Stumm (*Coll. Symp. Monograph*, IV. 253, 1920), Briggs (*J.P.C.* XXXII. 253, 1926), McBain (*J.A.C.S.* LI. 3294, 1929) and McBain and Peaker (*Proc. Roy. Soc.* A, CXXV. 394, 1929) have all obtained definite evidence of the increased conductivity of the liquid in close proximity to the interface. From conductivity measurements on optically smooth surfaces the latter concluded that the extra conductivity near the surface, ascribed to an excess of mobile adsorbed ions possessing the same mobility as in the bulk phase, would be equivalent to a packing of one-eighth of a unimolecular layer.

10. Surface reactions at the solid-liquid interface. The equilibrium of crystals in solution.

The fact that not only may the different surfaces of a crystal have different surface energies due to an alteration in the closeness of the packing of the molecules on the planes, but also that the molecules at the corners and edges of a crystal cannot adhere so strongly as those in the interior of the plane surfaces, gives us, as Gibbs (*Scientific Papers*, p. 325) has pointed out, a great deal of information on the mechanism of solution and growth of small crystals.

When a crystal is in equilibrium with its saturated solution there must be a kinetic fluctuation between the molecules of the crystal and those of the circumambient solution. The conditions of equilibrium at such an interface have been considered from a statistical point of view by J. A. Butler (*Trans. Farad. Soc.* XIX. 659, 1924) on the following lines. A molecule passing outwards from the surface of the crystal experiences first an attraction towards the surface and after a certain point an attraction into the liquid; there thus exists a balance point at which the two opposing attractions are equal. If a surface of a crystal containing N molecules per sq. cm. be placed in contact with a solution containing N_s molecules per c.c., and we consider a slice of solution at the surface of the solid in thickness equal to the mean free path of solute molecules in the solution and containing N_1 molecules, then the number of molecules moving towards the surface with a kinetic energy E per gram molecule at any instant is according to Maxwell

$$\phi = \frac{N'}{\sqrt{\pi}} \int_{E=\lambda}^{E=\infty} e^{-\frac{E}{RT}} d\sqrt{\frac{E}{RT}}\,.$$

The number of molecules escaping per second is equal to this quantity multiplied by the mean collision frequency, that is the mean velocity $\bar{v}$ divided by the mean free path $\bar{s}$. But $N_1 = N_s\,\bar{s}$, hence the number of solute molecules reaching the surface per second is

$$\theta = \frac{\phi \bar{v}}{\bar{s}} = \frac{N_s}{\sqrt{\pi}} \int_{E=\lambda}^{E=\infty} e^{-\frac{E}{RT}} v d\sqrt{\frac{E}{RT}}$$

or $\theta = N_s A \sqrt{T}\, e^{-\frac{\lambda}{RT}}$, where $A = \sqrt{\frac{R}{2\pi M}}\,.$

If in reaching the balance point from the interior of the solute a molecule does work W_1, then the number of molecules reaching the balance point from the solution per second is

$$\theta' = N_s A \sqrt{T}\, e^{-\frac{W_1}{RT}}\,.$$

The molecules at the surface of a crystal move only in a vibrational manner about an equilibrium position perpendicular to the crystal surface; the number escaping per second will evidently be proportional to (*a*) the number on the surface layer, (*b*) the number having at any instant a kinetic energy greater than λ per gram molecule, and (*c*) the number of times on an average the outward movement is repeated per second (assuming that the normal distribution of energy among the surface molecules is attained afresh for each new outward movement). That is, we replace the mean collision frequency by the vibration frequency ν and obtain

$$\theta = \frac{N}{\sqrt{\pi}} \nu \int_{E=\lambda}^{E=\infty} e^{-\frac{E}{RT}} d\sqrt{\frac{E}{RT}}\,.$$

On integration

$$\theta = N\nu \sqrt{\frac{RT}{\lambda\pi}}\, e^{-\frac{\lambda}{RT}} \left\{1 - \frac{RT}{2\lambda} + \frac{3R^2T^2}{4\lambda^2} - \dots\right\},$$

where if λ is very considerably greater than $\frac{RT}{2}$, this reduces to

$$\theta = N\nu\sqrt{\frac{RT}{\lambda\pi}}\, e^{-\frac{\lambda}{RT}}.$$

If in reaching the balance point a molecule from the surface layer does work W_2 per gram molecule, then the number of molecules reaching the balance point from the surface per second is

$$\theta'' = NA'\sqrt{T}\, e^{-\frac{W_2}{RT}}, \quad \text{where} \quad A' = \nu\sqrt{\frac{R}{W_2\pi}}.$$

In a saturated solution equilibrium between solution and deposition exists, or

$$\theta' = \theta''$$

or

$$NA'\sqrt{T}\, e^{-\frac{W_2}{TR}} = N_s A\sqrt{T}\, e^{-\frac{W_1}{RT}}.$$

Writing $C = \frac{N_s}{N_0} \times 1000$, where $N_0 =$ the Avogadro number,

$$\log_e C = \frac{W_1 - W_2}{RT} - \log_e \frac{AN_0}{1000A'\,N}$$

or

$$\log_e C = \frac{W_1 - W_2}{RT} - \log_e \frac{N_0}{1000\,N}\sqrt{\frac{W_2}{2M\nu^2}}.$$

$W_1 - W_2$ is evidently the heat of solution at saturation.

Since the edge molecules are held less tenaciously than those in the middle of the planes, we must suppose that at equilibrium several of the outermost layers of the molecules on the sides of crystal surfaces are incomplete toward the edges. This fluctuation is less as we proceed away from the edge towards the centre of the plane surface. To produce continued growth of a crystal it is necessary to build up the molecular planes at the surface. There is however a great difficulty in commencing a fresh plane, since until a molecular layer is formed the single molecules adhere to the underlying plane less tenaciously than those forming part of the underlying plane (in true equilibrium with the liquid). It necessarily follows that a certain small but finite degree of supersaturation is necessary to permit a crystal to grow.

The difference between the minimum growing concentration and the saturation equilibrium value represents the difference in the adherence of a molecule in a plane and one adhering to the plane surface.

For solution on the other hand no such difficulties occur. It has already been noted that the edges of the planes are already stripped under conditions of equilibrium; a small decrease in the concentration of the solution simply extends the edges farther towards the centre of the plane until it is stripped entirely. The mechanism of crystal growth thus presupposes a finite degree of super-saturation; this no doubt varies with the surface energies of the crystal faces and will probably be greatest for the surfaces for which σ_{sl} is least, whilst on solution of a crystal the degree of under-saturation necessary to produce a continued stripping of the surface will also be least for surfaces of low σ value. We thus arrive at the conclusion of Gibbs: "The effect of dissolving a crystal is therefore to produce a form which probably differs from that of theoretical equilibrium in a direction opposite to that of a growing crystal."

In actual processes of crystal formation and solution, forces other than surface forces may play an important part; thus in the solution of crystals it is necessary to dissipate the heat evolved on solution (see Nacken, *Neues Jahrbuch Min. Geol. Pal.* II. 133, 1915). Such dissipation may take place most readily at edges and corners. Again, a crystal undergoing solution in a nearly saturated solution will be surrounded by a saturated layer of solution. This layer being denser than the surrounding medium will sink to the bottom of the vessel and thus accelerate the normal process of solution. In this way also exposed edges may dissolve more rapidly than the plane surfaces.

11. Rate of solution at plane surfaces.

The rate of solution of solids in liquids is found to be a reaction of zero order provided that the concentration of the solution remains unchanged and the surface exposed to solution constant, as is indicated by the early experiments of Wenzel (*Lehre der Verwandtschaft*, XXVIII. 1777) and of Veley (*J.C.S.* LV. 361, 1889; *Phil. Mag.* CLXXXII. 279, 1891) on the rate of solution of metals in acids.

In the case of solution of a solid in a limited volume of solution the rate of solution will follow a unimolecular law; thus in the case of metals dissolving in acids, or salts in water, for a constant area of interface the rate will be expressed by the equation

$$\frac{dx}{dt} = k(a - x),$$

where a is the original concentration of the acid, a conclusion confirmed by Spring's experiments on the rate of solution of calcspar in hydrochloric acid. The rate of solution of solids has been examined in detail by Noyes and Whitney (*Zeit. physical. Chem.* XXIII. 689, 1897), Nernst (*ibid.* XLVII. 52, 1904), Brunner (*ibid.* XLVII. 56, 1904), Nernst and Merriam (*ibid.* LIII. 235, 1905) and others.

It was found that the solution of a solid consists essentially of two processes, the actual process of interaction of solid and solvent and the diffusion of the solvated solute away from the surface.

The crystal surface may be regarded as covered with a layer of saturated solution of a definite thickness through which the products have to diffuse. If the actual solvation of the solid proceeds rapidly in comparison to the process of diffusion the rate of solution will be essentially that of diffusion, and can accordingly be expressed by the Fick diffusion equation, the rate of solution per unit area of interface being given by

$$-\frac{dx}{dt} = D\frac{C_s - C}{\delta},$$

where D is the diffusion constant, C_s the saturated, C the actual concentration of the solution and δ the thickness of the diffusion layer. Experimental evidence in support of this point of view as to the mechanism of the process has been advanced by examination of the rates of solution of such substances as benzoic acid, lead chloride and silver acetate in water; also by the solution of magnesia in acetic, benzoic and hydrochloric acids. As examples may be cited the values given on p. 285 for the solution rate of small rods of magnesia rotating at a constant speed in the solvent.

The velocities of solution are evidently approximately proportional to the diffusivity and not to the acid strengths. The temperature coefficient of these processes is likewise small, being 1·25 for a rise of 10° C. of the same order as that for diffusion.

Solvent	Velocity constant k	Diffusion coefficient
Benzoic acid...	1·55	0·75
Acetic acid ...	2·05	0·95
HCl and $MgCl_2$	8·10	6·70

The values of δ the film thickness are found to vary with the nature of the reaction, but lie within the limits 0·02 to 0·065 mm. The film thickness is dependent on the speed of rotation n for the case of the solution of benzoic acid and of magnesium benzoate in water.

We may likewise obtain an estimate of the thickness of the adsorbed film by determining the maximum current density at which ions may be deposited at an electrode which is kept in rapid rotation. The ions being deposited must be regarded as migrating across a film of thickness δ from a concentration equal to that in the bulk of the electrolyte to a region of zero concentration under the applied electromotive force. Thus Ackerberg (*Zeit. anorg. Chem.* XXXI. 161, 1902) obtained $\delta = \cdot 095$ mm. from measurements on the rate of the electrolytic oxidation of oxalic acid. Fischer (*Elektrochemie*, p. 60) obtained the following values from data on the limiting current densities in the precipitation of copper at a rotating cathode:

n R.P.M.	δ in mm.
250	·0635
800	·0565
1100	·0510

Dushman (*J.P.C.* XIV. 885, 1910) found $\delta = \cdot 040$ mm. under similar conditions, whilst Brunner (*loc. cit.*) found that $\delta n^{\frac{2}{3}}$ was approximately constant.

The catalytic decomposition of hydrogen peroxide at the surface of platinum foil investigated by Bredig and Tetelow

(*Zeit. Elektrochem.* XII. 581, 1906) was found to obey a unimolecular law and the seat of the reaction was shown to be the thin saturated layer at the surface of the metal.

In some cases, e.g. the oxidation of hydrocarbons by potassium permanganate (Meyer and Saam, *Ber.* XXX. 1935, 1897), the hydrolysis of emulsions of esters in water (Goldschmidt, *Zeit. physikal. Chem.* XXXI. 235, 1899), and the dissolution of arsenious oxide (Drucker, *ibid.* XXXVI. 693, 1901), the actual chemical reaction between solvent and solute appears to be slower than the process of diffusion, and thus the rate of chemical action is independent of the diffusion coefficient.

The observations of Goldschmidt on the hydrolysis of esters are in contradiction to the data obtained by Norris and McBain (*J.C.S.* CXXI. 1362, 1922), who obtained the normal temperature coefficient of 1·5 and the $\delta n^{\frac{2}{3}}$ relationship for the saponification of oils and fats by aqueous alkali.

12. Crystallisation from solution.

In the rate of crystallisation of a substance from a supersaturated solution two independent factors have to be considered, firstly the rate of nucleus formation from which crystallisation may proceed and secondly the rate of growth of a nucleus once it is formed.

Nucleus formation.

As has already been noted (p. 253), the solubility of small crystals is greater than that of large ones; hence before a nucleus can act as a centre from which spontaneous crystallisation may proceed, it must possess a certain limiting size dependent on the surface energy of the solid and the degree of supersaturation of the solution. The spontaneous formation of such a nucleus can only take place in solution as the result of intermolecular collision. Adopting Langmuir's hypothesis of inelastic collision, each contact between two molecules of solute in a solution results in an adhesion for a definite although short period of time, the periods being in all probability somewhat longer than in the case of gases. In general the problem of adherence on collision in solution is complicated by the fact that both ions of electrolytes and molecules of non-electrolytes are solvated, and thus do not actually come in contact with one another. For orientated collision to take place so as to build up the elementary crystal lattice it is necessary to postulate either contact between unsolvated molecules or ions, or a movement of the solute particles towards one another within their solvated atmospheres which then merge into a common sheath. In the rapid condensation of metallic vapours it has likewise been noted (see p. 173) that adherence may result in the formation of an amorphous material which sinters to the crystalline state at a rate dependent on the mobility of the atoms within the mass. A somewhat similar phenomenon has been observed and investigated by von Weimarn (see p. 299) in the preparation of colloids from highly supersaturated solutions. The rate of formation of nuclei will however in general increase with increasing concentration of the solution. At any definite temperature the molecules are in thermal agitation by which intermolecular contacts are produced; at the same time the same agitation is the operative process by which rupture is caused between adhering molecules. Thus there will be a maximum rate of nucleus formation at a definite temperature; below which temperature the rate of intermolecular collision is decreased by the decrease in the thermal agitation of the molecules and the increase in the viscosity of the medium, eventual solidification to glasses taking place. Above this temperature, in spite of the increase in the rate of collision, the rate of disintegration of the micro-nucleus is increased.

The existence of such a maximum has been shown by Tammann (*Kristallisieren und Schmelzen*, p. 151) and a mathematical analysis has been made by Furkas (*Zeit. physikal. Chem.* cxxv. 236, 1927).

13. Rate of crystallisation.

If a crystal surface be exposed to a supersaturated solution, the surface will commence to grow. As has already been noted, the surface energy of a crystal is dependent not only on the nature of the substance but also on the packing in the space lattice; the rate of growth will thus vary with the crystal face, e.g. the faces of a crystal of the cubic class will possess different growth rates depending on whether the 100 or 111 face is exposed to the solution.

It was noted in the case of solution that frequently the rate of solution was apparently governed by the rate of diffusion of the solute through a saturated film of definite thickness. As a first approximation the growth of a crystal may be regarded as an analogous process, viz. the diffusion of the salt from a supersaturated solution through a saturated film to the crystal surface. Under these conditions the growth rate per sq. cm. would be given by the expression

$$-\frac{dx}{dt}=\frac{D}{\delta}(C_0-C_s),$$

where C_0 is the concentration of the supersaturated solution, C_s that of the saturated film.

The velocity of linear crystallisation has been determined in the case of fused solids by Tammann and his co-workers (*loc. cit.*), in supersaturated solutions by Marc (*Zeit. physikal. Chem.* LXI. 385, 1908; LXVII. 470, 1909; LXVIII. 104, 1909; LXXIII. 685, 1910; LXXV. 710, 1911; LXXIX. 71, 1912), Le Blanc (*ibid.* LXXVII. 614, 1911), and others.

The crystal growth rate has been found in many cases to be extremely rapid, more rapid than can be accounted for on the diffusion hypothesis; thus Tammann (*loc. cit.*) found for benzophenone a maximum crystallisation velocity of 2·4 mm. per minute (Walton and Judd, *J.P.C.* XVIII. 722, 1914). Much higher values, e.g. 6840 mm. per minute for water and 60,000 mm. per minute for phosphorus (Gernez, *C.R.* XCV. 1278, 1882), have been recorded. In some cases the rate was found independent of the speed of rotation of the stirrer and occasionally the reaction velocity followed a bimolecular law instead of the simple unimolecular expression which holds true for solution.

14. Influence of addition agents on rates of solution and crystallisation.

The rate of solution of crystals of potassium sulphate was found to be uninfluenced by the addition of many substances such as quinoline yellow to the solution by Marc and Wenk (*Zeit. physikal. Chem.* LXVIII. 112, 1910). Small alterations in the solution rates are however to be expected on the diffusion hypothesis if the extraneous material or "addition agent" affects the diffusion constant of the salt in the solution. Friend and Vallance (*J.C.S.* CXXI. 466, 1922) have shown a slight retardation in the rates of solution of potassium sulphate in solutions containing small amounts of agar and gelatine. The rate of solution of metals such as iron in acids is much retarded by the addition of many substances such as gelatine and agar (Friend and Dennet, Friend and Vallance) as is exemplified by the following figures for the retardation caused by the addition of small quantities of gum acacia added to normal hydrochloric acid in the solution of iron:

Gum acacia % added	Retardation %
0	0
0·001	0
0·01	40·8
0·05	45·1
0·10	60·4
0·20	62·5
0·50	70·8

The dilutions are too great to alter sensibly the diffusion constant of the medium, Friend suggests that the extraneous material or addition agent is selectively adsorbed and thus protects the iron from attack. An alternative explanation is the formation of an insoluble compound on the metal surface such as obtains in many cases of passivity.

In the converse case of crystallisation from a fused material or from a supersaturated solution the influence of addition agents is most marked. No regularity has been observed in the influence of soluble impurities on the formation of nuclei (Tammann, *loc. cit.*); the effect of the addition of powdered solids which occasionally act as nuclei has likewise not proved amenable to systematic classification although the criteria of isomorphism, e.g. identity or close approximation to identity in crystalline form, or the formation of mixed crystals hold true in cases where the supercooling is not great.

The effect of extraneous material on the linear velocity of propagation of crystal growth is marked and definite.

V. Pickardt (*Zeit. physikal. Chem.* XLII. 17, 1902) in his investigations on the lowering of the crystallisation velocity of fused benzophenone in the presence of various substances came to the conclusion that equimolecular proportions of the addition agents produced an identical lowering. According to Freundlich (*Kapillarchemie*, p. 448) this relationship only holds true for substances which possess identical constants in the Freundlich isotherm, the lowering of the velocity being due to adsorption of the addition agent on the crystal surface and is not occasioned by an alteration in the possible variables D or δ.

Similar observations on the retardation of crystallisation from solutions of salts such as potassium sulphate have been made by Marc (*Zeit. physikal. Chem.* LXVIII. 112, 1910; LXXIII. 708, 1910), who showed that the retardation was most marked in the presence of dyes, such as quinoline yellow, which were strongly adsorbed by the crystals. In the electro-deposition of metals in the presence of addition agents these materials can be detected in the electrolytically deposited metal.

The effect of such addition agents, which are strongly adsorbed, is in general not limited to an alteration in the velocity of crystalline growth, but frequently affects the crystal habit. The adsorbed material lowers the interfacial surface energy of the crystal and thus may permit the growth of those facets which normally possess too much interfacial energy to come into existence, e.g. octahedral crystals from sodium chloride in the presence of urea (Spangenberg, *Zeit. Kryst.* LXI. 189, 1925), dendrites from silver chloride in the presence of methylene blue, fine grained metal from the electrolysis of lead solutions in the presence of small quantities of gelatine and dendrites in the presence of relatively high concentrations (see Marc, *loc. cit.*, Reinders, *Zeit. physikal. Chem.* LXXVII. 680, 1911).

Cube facets may be developed on crystals of barium nitrate by addition of methylene blue (Walcott, *Am. Min.* XI. 272, 1920) or as shown by Saylor (*Coll. Sym.* V. 51, 1927) by the addition of other adsorbable cations, e.g. by addition of nitric acid. Saylor (*loc. cit.*) cites the interesting case of calcite and its two allotropic forms aragonite and vaterite. By the addition of increasing quantities of the strongly adsorbed bicarbonate ion, the more stable form of growth calcite may be suppressed and with a large excess only vaterite crystallises out. Alcohol which cuts down the adsorption of the bicarbonate ion permits of the growth of calcite even in the presence of excess $\overset{\prime}{H}CO_3$. Milligan (*J.P.C.* XXXIV. 1362, 1929) has likewise observed some interesting cases of selective adsorption of chlorazol sky blue F.F. on the 100 planes of potash alum and of azo dyes on the *b* 010 prism faces of potassium sodium tartrate, phloxine an eosine dye being adsorbed chiefly by the pinakoid *c* 001 plane.

A few cases have been recorded (Dreyer, *Zeit. physikal. Chem.* XLVIII. 487, 1904) where the effect of the addition agent on the crystallisation velocity is to be attributed to an alteration in the diffusion constant of the solute in the solution; thus the velocity of crystallisation of formanilide is increased and not decreased by the addition of methyl or ethyl alcohol to the fused salt.

15. The formation of suspensions.

The effect of dispersing a solid in a liquid is to produce a solid disperse phase in a liquid dispersion medium. Such colloidal systems are termed "sols," dispersoids, suspensoids or suspensions. Suspensions may be produced by condensation from soluble salts in solution or by the disintegration or dispersion of a massive solid phase. By these methods it is possible to prepare colloidal systems consisting of a solid dispersed in a medium to any requisite degree of concentration and dispersity. Such disperse systems will not however necessarily be stable when thus prepared and in order to obtain stable systems factors other than mere size which controls the magnitude of the thermal or Brownian agitation have to be considered. Most potent amongst these stabilising factors which form an important part of investigations in systematic colloid chemistry are the electrical charges on the dispersed particles produced in general by ionic reactions occurring at the surface of the dispersed material and the circumambient liquid. We find also that extraneous materials which are preferentially adsorbed at the solid-liquid interfaces and lower the interfacial surface tension exert a great influence on the stability of the suspension. The mechanism and influence of these factors on the stability of suspensions will be discussed later (Ch. VII) and we will here confine our attention to the general methods of procuring suspensions or disperse systems without special regard to their ultimate stability.

16. Methods of dispersion.

The formation of a colloidal suspension by the disintegration of a solid or the reforming of a stable colloidal solution from one in which the original suspension has undergone precipitation or agglomeration is frequently termed peptisation, a word introduced by Graham. This method of producing suspensions has been investigated in detail by Bancroft (*Second Report on Colloid Chemistry*, 1918) where he adopts Freundlich's interpretation of the mechanism of the process. On the adsorption of a liquid by a solid the surface energy of the solid is lowered and we may, according to Freundlich, regard the adsorbed film as one possessing a low surface tension on the liquid side and a high one on the other side; the adsorbed film will thus tend to disintegrate or peptise the solid substance. It is somewhat difficult to conceive of a film with a high and low surface tension on each side of it unless assumptions are made as to the thickness of the film. The process of disintegration of a solid may be regarded equally conveniently from a somewhat different point of view. That a crystal of a soluble salt dissolves in water may be considered as a demonstration that the cohesion between the molecules in the crystal is less than the adhesion of the water to the molecules constituting the surface of the crystal. As the quantity of salt in the water increases the adhesional forces between the salt water and crystal decrease until they become comparable with the intermolecular cohesion. Thus in strong solutions of electrolytes the formation of associated molecules, e.g. $(NaCl)_x$, $(BaCl_2)_y$, is by no means infrequent. In all those cases where the intermolecular forces holding the solid are sufficiently small or the adhesional forces between dispersion liquid and solid sufficiently great solution will take place. If the adhesional forces are but slightly greater than the cohesional forces, solution will not be complete but associated molecules or colloidal suspensions will be formed. Frequently mechanical methods of dispersion may be adopted and the resulting disperse phase "protected" from recoalescence by adsorption of a "protective" agent present in the solution.

The simplest cases of disintegration to a colloidal solution are those produced by immersion of a solid in a liquid, e.g. the disintegration of nitrocelluloses by means of amyl acetate. The solvent action of the medium is frequently greater at high temperatures than at low as noted by Lorenz in the dispersion of metals in contact with fused salts.

Bancroft cites cases in which disintegration is effected more readily in mixed solvents than by either solvent alone such as cellulose nitrate in ether alcohol mixtures. The interfacial surface tensions of such mixtures do not appear to have been measured.

Direct disintegration of ordinary chemical precipitates in water should be brought about by the addition of a solute which will be positively adsorbed by the precipitate in the solution. Such cases of positive adsorption should result in disintegration unless the cohesion of the precipitate be too great. No such cases of the addition of a non-electrolyte to water in effecting disintegration have been recorded although the addition of certain substances such as sugar and glycerine prevents the precipitation of certain hydrous oxides such as ferrous hydroxide where it is to be presumed that the internal cohesion is not great.

Not only may soluble non-electrolytes in a solution be adsorbed selectively by the material undergoing peptisation but frequently the adsorption of hydrated colloidal materials may take place. Although it can readily be demonstrated that substances like gelatine are adsorbed by and protect metals (and that they readily effect the disintegration of precipitates) yet no direct dispersive effect on metals themselves has been observed. Wegelin (*Zeit. Kolloid. Chem.* XIV. 65, 1914) has noted however that processes of mechanical disintegration of metals are greatly facilitated by the addition of gelatine. The metal particle which has adsorbed the gelatine is now less sensitive to precipitation by electrolytes and has in fact acquired properties more akin to an emulsion than to a suspension and is said to be "protected."

17. Protection of suspensions.

This decrease in sensitivity to electrolytes of a suspensoid by adsorption of a hydrated colloid from a solution provides a ready method for the estimation of the protecting power of these stabilising colloids. The coagulation of gold sols is associated with a marked change in colour from red to violet and has been employed by Zsigmondy (*Zeit. f. analyt. Chem.* XL. 697, 1901) as a standard for the estimation of protecting power which he expresses in terms of "gold numbers." The gold number of a protective colloid is that weight of colloid in milligrammes which will just permit the colour change in ten millilitres of a colloidal gold solution containing 0·0058 % of gold to occur on the addition of 1 m.l. of a ten per cent. sodium chloride solution.

The gold numbers of the various protective colloids vary greatly and indeed the method offers a means for the detection of substances otherwise not easily identified, e.g. the starches.

As typical of the gold numbers of various protective colloids the following values may be cited.

Albumen.	
White of egg	0·08
Albumin	0·1–0·3
Globulin	0·02–0·05
Ovomucoid	0·04–0·08
Crystalline albumin	2–8
Alkali albumin	0·0014–0·14

Starches.	
Wheat starch	4–6
Dextrin	6–12
Potato starch	25

Gum arabic		0·5
Gum tragacanth		2
Gelatine		0·005–0·01
Isinglass		0·01–0·02
Casein		0·01
Na oleate		0·4–1
Na stearate at	6° C.	10
„ „	100° C.	0·001
Stannic acid		∞

Disintegration to the colloid state may also be brought about by electrolytes. In general as has already been noted the ions of an electrolyte are not equally strongly adsorbed by a surface; owing to the preferential adsorption of one ion the surface acquires a charge of the same sign as the more strongly adsorbed ion, the cohesion between the particles is consequently lowered and although the interfacial surface tension is likewise reduced disintegration frequently results. The laws governing ionic adsorption will be discussed in connection with coagulation by electrolytes. It may be noted in passing that relatively insoluble electrolytes which are those to which the method of disintegration with the aid of electrolytes is most readily applicable, adsorb their own ions most markedly and in consequence salts containing a common ion are most effective disintegrating agents. Thus hydroxides will disperse the hydrated oxides of zinc, aluminium and chromium: both silver and chlorine ions will disperse silver chloride. Sulphides may be disintegrated with the aid of hydrogen sulphide and many oxides by the formation of basic salts with chloride or nitrate ions.

The redispersion of a sol which has been precipitated by the addition of an electrolyte may also occasionally be effected by the removal of the precipitating agent through washing; thus certain precipitates such as silver chloride, zinc sulphide and copper ferrocyanide are readily redispersed in water where the precipitating salts are removed by thorough agitation and filtration.

18. Electrical dispersion methods.

Two methods of dispersion by electrical methods have been developed; one first investigated by Davy depends on the fact that where the current density at cathodes in suitable electrolytes exceeds a certain critical value the cathode undergoes disintegration. Davy noted the formation of a purple red suspension of tellurium by the cathodic disruption of a rod of the metal. Müller (*Zeit. Elektrochem.* XI. 521, 1905) confirmed this observation of Davy's and extended the method to selenium and sulphur by covering a platinum cathode with the fused elements. Metals such as lead, tin, bismuth, thallium, arsenic, antimony, and mercury are readily dispersed cathodically by electrolysis in alkaline solution at high current densities (Bredig and Haber, *Ber.* XXX. 2741, 1898; Haber and Saeck, *Zeit. Elektrochem.* VIII. 245, 1905; *Zeit. anorg. Chem.* XXXIV. 286, 1903).

The mechanism of cathodic disintegration involves the formation of a metal alloy with a cation only deposited at high current densities and a large impressed electromotive force. Thus the disintegration of a lead cathode in alkaline solution is due to the formation of a lead sodium alloy which subsequently reacts with the water yielding a fine black dispersed lead suspension. This electrical dispersion occurs still more readily in fused solutions as noted by Lorenz owing to the more effective disintegration caused by the fused electrolytes in comparison with water. Of more general utility is the arc dispersion method introduced by Faraday (*Proc. Roy. Inst.* 310, 1854) and developed by Bredig (*Zeit. Elektrochem.* IV. 514, 1899; *Zeit. physikal. Chem.* XXXI. 288, 1899). By forming an arc under various dispersion media such as water or organic liquids between wires formed of the metal, dispersion of the metal may be effected. A current of some ten amperes with a potential fall of some forty volts is usually sufficient to effect the dispersion of most metals such as platinum, gold, palladium, iridium and silver. Many metals in water give rise only to hydroxides or oxides detectable by X-ray examination (Freundlich and Kroch, *Zeit. physikal. Chem.* CXXIV. 155, 1926) when dispersed in this manner, e.g. aluminium, thallium, iron, copper and zinc, whilst the presence of small quantities of hydroxylions is desirable for producing fine dispersions of the more noble metals.

The thermal effects of the arc not only in promoting the oxidation of readily oxidisable dispersed metals but also in decomposing the dispersion media when organic liquids are employed were a serious objection to the method and attempts to improve the method which were finally successful were made by Svedberg (*Ber.* XXXVIII. 3616, 1905; XXXIX. 1705, 1906; *Methoden zur Herstellung kolloider Lösungen*, 1909). By increasing the area of the electrodes and insertion of a condenser in parallel with the arc gap and reducing the current density of the arc Svedberg noted a great improvement in the purity of the metals dispersed in this way but decomposition of the medium was still marked when highly reactive metals such as the alkalis, or catalytic metals such as cobalt, nickel or platinum were employed, whilst several "hard" metals, e.g. aluminium, did not disperse readily when subjected to this treatment. By using an oscillating discharge from an induction coil as source of current and a condenser in parallel with the electrodes a great improvement in the purity of the dispersions or sols was achieved. By this method dispersions of various metals and metalloids in diverse media such as water, organic alcohols, ketones, ethers, chloroform and hydrocarbons have been prepared, the best results being obtained with short arcs in a system of low resistance, small inductance and large capacity.

The mechanism of colloid production by means of these immersed arcs or sparks has not definitely been established. It has been noted that disintegration in the direct current arc occurs mainly at the cathode and it has indeed been suggested that these electrically produced dispersions are not the primary product of cathodic disruption but rather the result of an evaporation and secondary condensation and aggregation of metal vapour.

19. Methods of condensation.

The methods of disintegration rely entirely upon increasing the dispersity of a solid, which process can, at least theoretically, be stopped at any instant, resulting in the formation of a suspension of definite dispersity but one that is not necessarily stable. The processes of suspension formation by methods of condensation on the other hand are more complicated, owing to the fact that unless the resulting colloidal suspension possesses at least some degree of stability the process of condensation once set in operation will not cease but proceed until the transformation to the macrocrystalline structure is complete.

The conditions of effecting condensation so as to produce a colloidal solution have been investigated in detail by von Weimarn (*Grundzüge der Dispersoidchemie*, 1911). The production of a colloidal solution by condensation according to von Weimarn is the result of two opposing forces in crystal formation, one the inter-atomic forces of the material which tend to impart to the material its crystalline characteristics and the other the molecular kinetic processes coming into play at the crystal surfaces; this factor is dependent not only on the nature of the disperse material but also on the activity of the dispersion medium in relation to the disperse phase. Thus, according to von Weimarn, colloidal solutions whether dispersions, gelatinous precipitates or gels are in reality crystalline and built up of small crystals which under suitable conditions may link up one with another to form a network in which the dispersion medium may be retained. The conditions for forming colloidal solutions are thus dependent on the formation of small crystals which as has been pointed out are produced in solutions in which nucleus formation readily obtains, but where the subsequent growth of the minute nuclear crystals is relatively small.

The rate of nucleus formation is dependent both on the actual amount of solute in the solvent and on its solubility; thus if a solution of sodium malonic ester in ligroin be added to a solution of chloracetic ester in the same solvent, by interaction an amount S of sodium chloride will be formed which by choice of suitable concentrations will exceed the actual solubility of sodium chloride in ligroin (s) by an amount $S - s$ or P. The rate of nucleus formation is in the first instance dependent on the velocity of initial condensation or the specific supersaturation

$$\frac{dn}{dt} = R\frac{S - s}{s} \quad \text{or} \quad R\frac{P}{s} = U,$$

whilst the subsequent rate of growth of the nuclei once formed in the above manner is dependent as shown by Noyes and Whitney (see p. 284) on the diffusion coefficient as well as the absolute supersaturation of the solution x

$$\frac{dx}{dt} = \frac{D}{\delta} Sx.$$

These two equations thus define, according to von Weimarn, both the nature of the disperse phase produced by condensation and the life of the disperse in the form produced at the moment of separation.

The specific supersaturation U which determines the nature of the disperse phase must possess a large value for the rapid formation of many nuclei which is the condition for separation in the suspension or gel form. If the saturation concentration s be great a large amount of disperse phase will be produced for big values of U and we shall obtain a phase separation containing a great number of nuclei at small distances apart, i.e. conditions favourable to the formation of a bridged network or a gelatinous precipitate. If on the other hand the saturation concentration s be small the disperse phase separating for large values of U will be highly dispersed, conditions favourable for true dispersion or suspension formation.

With the guidance of the above considerations von Weimarn has been able to prepare a great number of inorganic salts in the colloidal form. As typical of a gradual transformation from the crystalline to the colloidal state of aggregation with increasing values of U, the following values for barium sulphate prepared by the interaction of solutions of barium thiocyanate and manganous sulphate may be cited.

Concentration of reagents in normality	$S - s$	$U = \frac{S - s}{s}$	Nature of precipitation
·00005–·00014	0–·0006	0–3	No precipitate in a year
·00014–·0017	·0006–·0096	3–48	Slow precipitation $U = 8$. Momentary suspension stage at $U = 25$. Complete separation in months to hours as large crystals
·0017–0·75	·0096–4·38	48–21,900	Precipitation in a few seconds at $U = 48$. Beyond this instantaneous precipitations in crystal skeleton form. At $U = 21,900$ crystals are barely recognisable
0·75–3	4·38–17·51	21,900–87,500	Immediate formation of "amorphous" precipitates
3–7	17·51–40·9	87,500–204,500	Clear cellular jelly

From these data it is evident that a momentary "suspension" stage is obtained for values of U equal to 8–25, but on attempting to increase the U values to obtain more definite persistence of the suspension a gel is formed; thus to prepare a colloidal suspension of barium sulphate a medium must be employed in which U values of 8–25 may be obtained at lower concentrations, i.e. we must reduce the actual solubility of barium sulphate. By performing the double decomposition in alcohol water mixtures in which the solubility of barium sulphate is small a clear stable suspension may in fact readily be formed.

The theory of von Weimarn thus accounts fully for both the appearance and stability of the colloidal phases in processes of condensation, but it is still an open question whether in fact the colloidal particles are entirely crystalline when prepared in this manner. The investigations of Scherrer (*Gött. Nachrichten*, 1918) with the Röntgen rays on colloidal gold and silver have indicated that they undoubtedly contain crystals, but it is more than probable that the individual particle does not consist of one crystal but rather consists of an aggregation of minute crystal elements held together by surface tension and possessing a marked surface energy; such a composite particle could readily undergo transformation in size by aggregation or disintegration and could at the same time both by a process of solution and reprecipitation or by thermal agitation similar to the process of sintering be converted into the truly crystalline form possessing but little specific surface energy.

Methods of condensation in which protective colloids are employed, thus effecting condensation in the presence of a disintegrating agent, are largely employed for the preparation of stable suspensions; thus the precipitation of gold, platinum and palladium in the presence of gum arabic or the protalbic and lysalbic acids of Paal by means of reducing agents such as hydroxylamine, hydrazine, or formaldehyde readily results in the formation of remarkably stable suspensions.

CHAPTER VII

DIFFERENCES OF POTENTIAL AT INTERFACES

1. Origin of potential differences.

The galvanic cell.

The electric potential throughout the body of a homogeneous phase is constant but the possibility of obtaining an electromotive force from the terminals of a cell consisting entirely of homogeneous phases and their interfaces proves that in general there exist differences of potential across the latter. The interfacial potential difference is most readily detected when one of the phases is a metal as in the Volta pile. It is of importance to know the distribution of this potential, whether it is sharply confined to the interface or whether it extends some distance into either or both phases. In 1860 Sir W. Thomson drew the analogy between the potential across a polarised metal electrode and that across a charged condenser. This concept was extended by Varley (*Proc. Roy. Soc.* A, XIX. 243, 1870) who measured the capacity of a platinum electrode in dilute acid and the idea was developed by Helmholtz (*Wied. Ann.* VII. 337, 1897) who regarded the interfacial potential as extending between two plane sheets of charge, one situated in the metal surface and the other parallel to it in the electrolyte.

More recent work shows that the double layer is not so rigid as at first supposed, but that the layer of charge, at any rate in the electrolyte, extends to some distance from the interface.

The dependence of the potential difference between a metal and a solution containing its n valent ions, as shown originally by Nernst, takes the form

$$V = -\frac{RT}{nF}\log\frac{P_{\mathrm{M}}}{fc_{\dot{\mathrm{M}}}},$$

where $fc_{\dot{\mathrm{M}}}$ is the ionic activity of the electrolyte and P_{M} the electrolytic ionic solution pressure, a characteristic, according to Nernst, of the metal alone. Attempts have not been lacking to express the "ionic solution pressure" of a metal in terms of more definite and rational physical concepts.

Smits (*Theory of Allotropy*, ch. VII) attributes the potential to the difference in the relative solubilities of metallic ions and electrons. It is difficult to attach much physical meaning to the solubility of electrons in an electrolyte but that the polar water molecules may dissolve positive metal ions from off the surface of a metal gives us a physical interpretation of the origin of the Nernst solution pressure. Butler (*Trans. Farad. Soc.* XIX. 728, 1923) adopting this view has developed from kinetic considerations an expression for the E.M.F. of a galvanic cell

$$V = \frac{U}{nF} + \frac{RT}{nF} \log \frac{AN_0}{1000A'N'} + \frac{RT}{nF} \log fc,$$

where U is the heat of solution of the metallic ions and A and N quantities defining the statistical conditions.

Other attempts have been made notably by Langmuir (see also Heyrovsky, *Proc. Roy. Soc.* A, CII. 677, 1923, and Rideal, *Trans. Farad. Soc.* XIX. 1, 1924) to derive expressions involving the ionisation potentials or work functions of the metals, as well as the ionic solution heats, adopting the following cycle.

$$\begin{tikzcd}
M\text{ vapour} \arrow[r] & M\text{ ions} + \text{electrons} \arrow[r] & N\text{ ions} \arrow[r] \arrow[d] & N\text{ vapour} \\
\begin{array}{c}\text{Metal}\\ \text{M}\end{array} \arrow[u] & \begin{array}{c}\text{Solution}\\ \dot{\text{M}}\text{H}_2\text{O}\end{array} & \begin{array}{c}\text{Solution}\\ \dot{\text{N}}\text{H}_2\text{O}\end{array} & \begin{array}{c}\text{Metal}\\ \text{N}\end{array} \arrow[u]
\end{tikzcd}$$

In general the thermodynamic potential of a constituent which is electrically neutral may be said to depend only on its concentration and its environment, but if it is an ion the electric potential of the phase must also be considered.

If the electric potential of the electrolyte be taken as zero and that of the metal as V in volts the thermodynamic potential of the metallic ions will be

$$\begin{aligned} \mu_{\dot{\mathrm{M}}} &= k_e + RT \log c \text{ for the electrolyte} \\ &= k_m + 96{\cdot}5 \,.\, 10^{10}\, nV \text{ for the metal,} \end{aligned}$$

where k_e represents the environment in the electrolyte and is only independent of c when the latter is small, $96{\cdot}5 \,.\, 10^{10}\, n = a_n$ is the charge on a grm. ion and k_m embraces both the concentration and the environment in the metal and is evidently independent of c.

Hence $$V = \frac{RT \log c - (k_m - k_e)}{96{\cdot}5 \,.\, 10^{10}\, n}.$$

In this relation $k_m - k_e$ is proportional to the logarithm of Nernst's "ionic solution pressure" and is seen to depend on the properties both of the electrolyte as well as of the metal as has been indicated above.

In a galvanic cell on closed circuit there are in general two metal/electrolyte interfaces, one liquid/liquid and one metal/metal interface all possible sources of potential differences. The early work of Volta on metal/metal contact potentials led him to ascribe to this interface the source of potential of the galvanic cell, but the work of Ritter, Faraday and Favre showed conclusively that the electrical energy was derived from the chemical changes occurring at the metal/electrolyte interfaces. This was in apparent conflict with the contact theory and accounts of the controversy have been given by Ostwald (*Elektrochemie, ihre Geschichte und Lehre*, Leipzig, 1890) and by Langmuir (*J. A. Electrochem. Soc.* XXIX. 125, 1916). Since the contact potential between dissimilar metals is greatly influenced by traces of adsorbed gases or oxide present on the metallic surfaces, supporters of the chemical theory maintained that the Volta contact potential was itself due to chemical action, a view strengthened by Le Roux' erroneous conception of the Peltier effect. He considered that the heat liberated or adsorbed at a metal/metal junction divided by the current passing gave the contact potential, which on this view could not exceed a few millivolts. Helmholtz and Lord Kelvin showed that the Peltier effect is not a direct measure of the total contact potential but is related to the temperature coefficient of the contact potential by the equation

$$V_{\text{Peltier}} = T\frac{dV_{\text{contact E.M.F.}}}{dT}.$$

This together with the success of the Nernst hypothesis in explaining the variation in the E.M.F. of a cell with changing concentration of the electrolyte led to general acceptance of the chemical theory.

Evidence from a study of thermionic and photoelectric emission indicates that the electron affinity ϕ is an intrinsic property of a metal. If two metals are placed in contact the metal with the smaller ϕ value will loose electrons and a potential difference will be created between the metals equal to

$$\Delta V = \phi_2 - \phi_1 .$$

As pointed out by Langmuir there is a marked correspondence between the order of electron affinities and the electrochemical series and the values of $\phi_2 - \phi_1$ are of the same order as the E.M.F.'s of galvanic cells. Thus in a Daniell cell

$$\phi_{\text{Cu}} - \phi_{\text{Zn}} = 4{\cdot}0 - 3{\cdot}4 = 0{\cdot}6 \text{ volts}$$

compared to the observed E.M.F. in normal solutions of 1·10 volts. The variation of E.M.F. of a cell with concentration of electrolyte indicates that part of the electromotive force has its seat at the metal/electrolyte boundaries, but it is clear that the contact differences at the metal/metal interfaces must be considered in any complete theory of the galvanic cell.

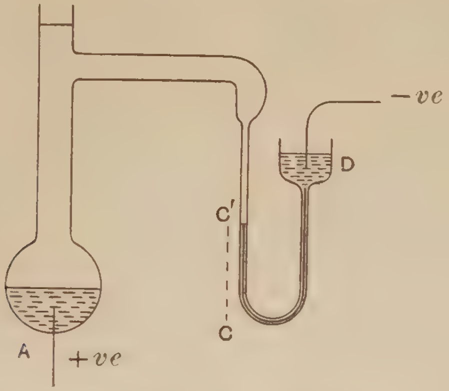
2. Electro-capillarity.

A change in the electric potential across an interface is accompanied by a change in the surface energy and if as in the case of mercury or gallium in contact with a solution the interface be fluid then the relationship between the interfacial potential and the surface energy can be measured directly.

The dependence of the surface tension on the electric potential across the interface was first established by Lippmann (*Ann. de Phys.* CLXXIX. 494, 1875) who studied the behaviour of a mercury surface in contact with dilute sulphuric acid and as a result devised the capillary electrometer.

This instrument consists essentially of a cell with a large mercury surface as anode and as cathode a mercury thread in a capillary tube CC'. As electrolyte, Lippmann used dilute sulphuric acid.

If the solution contains oxygen it reacts with the mercury on standing, producing a small quantity of mercurous sulphate which renders the anode unpolarisable. We have already noted that the height DC' between the mercury in the reservoir and the capillary electrode surface is a measure of the interfacial surface tension. If an external E.M.F. be imposed upon the cell the mercury meniscus in the arm CC' will be observed first to fall to a minimum value and then to rise again with increasing



applied E.M.F. On plotting the alteration of the interfacial surface tension against the applied E.M.F., Lippmann obtained a curve which within the limits of accuracy of his experiment was parabolic and rose to a well-defined maximum value.

On the assumption that the alteration in surface energy on passing a charge across the interface was purely electrostatic he deduced the relationships

$$-\frac{d\sigma}{dV} = \epsilon \text{ and } -\frac{d^2\sigma}{dV^2} = c,$$

where ϵ is the electrical capacity of the surface at constant potential, i.e. the quantity of electricity which crosses the interface when the area is increased by unity, the potential V remaining constant, c is the electrical capacity in the usual sense, i.e. the quantity of electricity necessary to increase V by unity, the area remaining constant. It is evident that c remains constant over the range where the V, σ curve is truly parabolic. We have seen that according to Helmholtz the interfacial potential extends between two parallel sheet-like boundaries and can be expressed by the equation

$$V = 4\pi M,$$

where M is the electric moment of the interface or if ρ is the density of charge on the surface and δ is the distance across the double layer

$$V = 4\pi\rho\delta.$$

In 1881 (*Monatsheft der Akad. Preuss.* p. 2, 1881) he applied this conception to the electro-capillary phenomena observed by Lippmann and by Quincke and identified the electrical capacity ϵ of Lippmann's equation with the charge ρ on the mercury surface.

Thus a mercury surface in contact with sulphuric acid on this view possesses a positive charge and situated a small distance from it in the solution is an equal sheet of negative charge probably caused by the anions of the electrolyte. The positive charges on the mercury surface will mutually repel one another and so decrease the surface tension*. On applying an increasing

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* The mutual potential energy of a plane network of doublets is dependent on the nature of the packing of the doublets. The case both for a square and for a triangular network has been investigated by Topping (*Proc. Roy. Soc.* A, CXIV. 68, 1928) who finds $\phi = \frac{1}{2} n^{5/2} \mu^2 K$, where n is the number of doublets per sq. cm., each of vertical moment μ. The constant $K = 9{\cdot}034$ for the square and $8{\cdot}893$ for the triangular packing.

We have noted that various equations of state have been proposed for two-dimensional gases and vapours both on liquid (Ch. II) and on solid surfaces (Ch. V), the Traube equation $FA = RT$ holds only for very small ranges of pressure; under normal conditions the equation of Volmer $F(A - B) = RT$ or of Rideal and Schofield $F(A - B) = iRT$ gives more satisfactory agreement. It has been mentioned that, as Magnus suggested, a two-dimensional analogue of the Van der Waals equation $\left(F - \frac{a}{A^2}\right)(A - B) = RT$ might be employed, where $\frac{a}{A^2}$ is the two-dimensional repulsion in contrast with the two-dimensional attraction of gases. Magnus considers this repulsion purely electrical in origin due to the mutual interaction of these orientated dipoles—and evaluates this potential to

$$\Phi = \frac{2{\cdot}37 N^2 \mu^2}{Ad} \text{ per grm. mol, where } A = Nd^2,$$

or $\Phi = 2{\cdot}37 A \mu^2 n^{5/2}$ which differs from that obtained by Topping only by a numerical constant.

The lateral repulsion per cm. $\frac{a}{A^2}$ is given by $-\frac{d\phi}{dA} = \frac{2{\cdot}37 N^2 \mu^2}{A^2 d}$ or $2{\cdot}37 \mu^2 n^{5/2}$.

Magnus gives the following data for two adsorption isotherms on charcoal negative potential to the surface the positive charge on the surface is diminished, becomes zero, and finally negative in sign with a corresponding increase and subsequent decrease in the surface tension. Thus according to this conception when $\frac{d\sigma}{dV} = 0$ at the maximum of the surface tension the electrical double layer has disappeared and there is no potential difference between the mercury and the solution.

Experiments with a dropping electrode by Varley (*Phil. Trans.* A, CI. 129, 1871), Paschen and Smith and Moss (*Phil. Mag.* XV. 487, 1908), showed that when an insulated mass of mercury was allowed to drop rapidly through a solution it always took up the potential corresponding to the maximum surface tension of the electro-capillary curve.

The behaviour of the dropping electrode could be explained on Nernst's hypothesis if the concentration of the mercury ions in the solution were such that their osmotic pressure was equal to the electrolytic solution pressure of the dropping mercury; the

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including the calculated value of a and a comparison with the saturation "constant" of the Langmuir isotherm.

	p mm.	$FA \times 10^{-6}$ obs.	$FA \times 10^{-6}$ calc.	$ka \times 10^{-9}$	Langmuir's saturation constant
T. 273°	84·2	34·4	35·3	1·76	92·8
	109·3	37·4	38·9	1·70	83·8
	216·6	50·2	50·6	1·85	68·6
	344·3	61·8	61·8	1·90	58·4
	440·0	68·6	69·3	1·83	52·6
T. 298°	86·2	25·1	24·6	1·33	103·0
	89·9	25·3	24·7	1·34	101·3
	146·2	28·8	28·3	1·31	95·7
	222·0	30·7	30·7	1·20	74·2
	368·7	37·0	37·0	1·20	68·2

On liquid surfaces however it is clear that the lowering of the surface energy cannot be due solely to dipole repulsion and it appears more than probable that two-dimensional adhesional forces as well as the electrical repulsive term for polarisable dipoles in different states of orientation and aggregation have to be taken into consideration.

drop would neither acquire nor lose mercury ions in its passage through the electrolyte; thus a dropping electrode, or a mercury meniscus at the maximum of surface tension, should be an electrode of "zero" potential. The potential of a decinormal calomel electrode against the dropping electrode is *ca.* 0·56 volts. This simple view is not correct since it has been found experimentally that the shape of the electro-capillary curve and the potential of the maximum of surface tension both vary with different electrolytes. The potential of the dropping electrode is also altered; but for any one electrolyte the potential taken up by the dropping electrode is always that which corresponds to the maximum of the electro-capillary curve in that electrolyte.

Before discussing the anomalies obtained with different electrolytes we will consider the phenomena from the point of view of adsorption.

By suitable choice of the dividing surface it has been shown (p. 48) that the equation of Gibbs reduces to the form

$$d\sigma = -\Gamma d\mu.$$

If the component of thermodynamic potential μ be an ion carrying a charge a_n and the electrical potential of one phase, e.g. the mercury be changed by dV, then in order to maintain equilibrium there must be a corresponding change in the thermodynamic potential of the component such that

$$d\mu = a_n dV$$

and the above equation becomes

$$-\frac{d\sigma}{dV} = a_n\Gamma.$$

The nature of the component Γ depends upon the arbitrarily chosen position of the dividing surface. Gibbs placed the dividing surface so that the surface excess of mercury was zero and expressed Γ in terms of the surface concentration of hydrogen. Warburg (*Wied. Ann.* (9), XLI. 1, 1890) expressed Γ in terms of the surface concentration of mercury ions and showed the relation between this and the Lippmann-Helmholtz theory by identifying Γ with the charge on the mercury surface, or

$$\frac{d\sigma}{dV} = a_{\overset{+}{\mathrm{Hg}}}\,\Gamma_{+} = -\epsilon.$$

On this view the concentration of the adsorbed mercury ions Γ_{Hg}^{+} is identical with Lippmann's electrical capacity at constant potential. Schofield (*Phil. Mag.* L. 641, 1926) placed the dividing surface so that there was no surface excess of mercury ions and expressed Γ in terms of the surface excess of electrons. This has been criticised by Frumkin (*Ergeb. der exact. Wissenschaft.* VII. 1928) and Butler (*Proc. Roy. Soc.* A, CXIII. 594, 1927) on the grounds that it leads to an illusory result, since with this choice of dividing surface the surface concentration of electrons cannot be identified with the charge on the double layer.

3. Experimental verification of Lippmann's equation.

An experimental verification of Lippmann's equation has been carried out by Frumkin (*Zeit. physikal. Chem.* CIII. 56, 1922) and by Schofield (*Phil. Mag.* I. 641, 1926).

Frumkin using a dropping electrode similar to that employed by Varley measured the current caused by the mercury dropping through the various solutions. Knowing the number and area of the drops the density of the charge on the mercury surface was obtained. He also measured $\frac{d\sigma}{dV}$ for a mercury surface in these solutions and from this by means of Lippmann's equation calculated ϵ. As shown in the following table the calculated and experimental values are in good agreement.

Solution	ϵ micro-coulombs/cm.^{2}	$d\sigma/dV$ micro-coulombs/cm.^{2}
n-NaCl with Hg_2Cl_2	47	50
n-KOH with HgO	17	21
$2n$-H_2SO_4 with Hg_2SO_4	39	39
n-KNO_3 + ·01n-KI with KI . HgI_2	90	86
n-KOH + $(C_2H_5)_2O$ with HgO	− 1·3	− 1·5

Schofield actually measured the amount of mercurous salt which was removed from a solution by an expanding mercury surface and compared this with the value of Γ calculated with the aid of Gibbs' and Lippmann's equation.

He found it easier in practice to test this relation by determining the increase in concentration of a solution flowing steadily over a mercury surface into which drops having previously come to equilibrium with the solution coalesced. The drops were counted by means of a rotating disc with radial slits mounted on a Rayleigh Wilberforce synchronous motor. By finding the weight of a given number of drops the area of each drop and hence the area removed per second were calculated. The number of grm. ions thereby thrown off into the solution as it flowed past was found by adjusting a current which, flowing between a still mercury surface as anode and a platinum foil in a side tube, caused an alteration in the mercurous ion concentration to yield the same increase, in E.M.F. Potentiometer observations were made to detect changes in mercurous ion concentration. The following table shows the agreement between the observed adsorption and that calculated from the slope of the corresponding electro-capillary curve.

E.M.F. (function of $C_{Hg^{\cdot\cdot}}$) millivolts	Γ directly measured grm. equivalents/cm.^{2} × 10^{10}	Γ calculated from slope of capillary curve, i.e. by Gibbs' equation grm. equivalents/cm.^{2} × 10^{10}
18·0	4·23	4·10
30·5	3·69	3·55
42·0	3·10	3·20

It thus appears that the surface concentration calculated with the aid of the Gibbs equation is equal on the one hand to minus the surface charge found by Lippmann's equation from the slope of the electro-capillary curve and on the other hand to minus the number of grm equivalents of mercury ions taken up by an expanding surface or thrown off by a contracting one.

4. Variation in the form of the electro-capillary curve.

The investigations of Rothmund (*Zeit. physikal. Chem.* XV. 1, 1874), Smith (*Phil. Trans.* A, CXCIII. 70, 1900) and of Gouy (*Ann. Chim. Phys.* (7), XXIX. 145, 1903) have shown that whilst the form of the electro-capillary curve at a mercury dilute sulphuric acid interface is almost exactly parabolic, in other electrolytes the form is greatly modified as is shown by the following data.

$V_{\text{max.}} - V_1$ in volts	δ from the expression $\delta = \frac{V_{\text{max.}} - V_1}{4\pi\epsilon}$ in Å. in the following electrolytes			
	H_2SO_4 (16 %)	KNO_3 M	Na_2SO_4 $\frac{M}{20}$	KI $\frac{M}{10}$
+ 1·0	·241	—	—	—
+ ·8	·321	—	—	—
+ ·6	·338	·312	·232	—
+ ·4	·324	·302	·236	·058
+ ·2	·295	·260	·264	·120
− ·2	·278	·310	·372	·201
− ·4	·339	·375	·413	·273
− ·6	—	·410	·445	·338
− ·8	—	·472	·468	·376
− 1·0	—	—	·479	·384
− 1·2	—	—	·483	—
− 1·4	—	—	·475	—

Gouy (*Ann. Chim. Phys.* VIII. 291; IX. 75, 1906) likewise noted a change in the position and form of the curve on the addition of organic substances to the electrolyte. This has led to a considerable modification of the simple theory of Helmholtz and the importance of "pure" adsorption has been emphasised. It was considered by Gouy (*C.R.* CXXXI. 939, 1900) that additional ions will be present on the surface if they are capillary active, so that at the maximum of the electro-capillary curve there may still be a considerable potential difference between the solution and the mercury due to this layer of capillary adsorbed ions.

Capillary active anions are more readily adsorbed on a positive surface and are thus more effective in depressing the rising or positive branch of the electro-capillary curve. Similarly active cations are more readily adsorbed on the descending or negative branch of the curve. Neutral molecules as shown by Gouy are most effective in the region of the maximum of the curve where the surface charge is a minimum. Attempts to achieve a quantitative interpretation of these results have been made by Frumkin (*Ergeb. der Naturwiss.* VII. 1928), and by Butler (*Proc. Roy. Soc.* A, CXII. 129, 1926; CXIII. 594, 1927; CXXII. 399, 1928).

An early attempt to explain the anomalies obtained in inorganic solutions such as iodides and cyanides was made by

Krüger (*Zeit. Elektrochem.* XIX. 681, 1913) on the assumption that the mercury salts were adsorbed at the interface. He modified Lippmann's equation to the form

$$-\frac{d\sigma}{dV} = \epsilon + F(k-1)c\delta,$$

where c is the bulk concentration of the mercury salt, δ the thickness of the double layer and k the distribution of the salt between the surface layer and bulk of the solution. Whilst this view explains the fact that electrolytes forming complex salts with the mercury give a greater displacement for the curve than for that observed with sulphuric acid yet as noted by Frumkin (*Phil. Mag.* XL. 803, 1920) the additional term is not sufficiently large to account for the observed anomalies and is inapplicable to non-electrolytes.

Both Frumkin and Butler derive an expression in which the second term represents the excess concentration of adsorbed ions; where mercury ions are specifically adsorbed this becomes

$$-\frac{d\sigma}{dV} = a_{\overset{+}{\mathrm{Hg}}}\Gamma_{\overset{+}{\mathrm{Hg}}}' + 2kV,$$

where $\Gamma_{\overset{+}{\mathrm{Hg}}}'$ is the additional amount of mercury ions specifically adsorbed at the interface (above that which corresponds to the electron charge on the double layer) and $2kV$ corresponds to the $-\epsilon$ of Lippmann's equation. At the maximum of the electrocapillary curve where $\frac{d\sigma}{dV} = 0$, ϵ is not zero but is equal to $-a_{\overset{+}{\mathrm{Hg}}}\Gamma_{\overset{+}{\mathrm{Hg}}}'$. We can thus understand why mercury dropping into a "null" solution (i.e. a solution in which the surface tension is a maximum) produces no change in the concentration, for the number of mercury ions transferred from the expanding mercury surface into the solution to give the mercury surface the required charge is just equal to the amount which is specifically adsorbed.

Butler develops a kinetic treatment to the adsorption of the ions and obtains an expression for the lowering of the surface tension in terms of the potential V and the amount initially adsorbed. If the work done on adsorption of an ion is a fraction α of the total work done on transfer of an n valent ion nFV and if Γ_0 is the amount adsorbed when $V = 0$, Butler obtains the expression

$$\sigma - \sigma_0 = - a_{\overset{+}{\text{Hg}}} \Gamma_0 \frac{RT}{\alpha n F} e^{-\frac{\alpha n F V}{RT}} .$$

This expression is found to apply with some exactness to the experimental data of Smith (*Phil. Trans.* A, CXCIII. 48, 1899) on potassium iodide and cyanide. It is found that $\alpha = 0{\cdot}122$, so that the electrical work of adsorption of the anions may be considerably less than the total potential difference across the interface.

5. The adsorption of neutral molecules.

We have seen that Gouy noted that capillary active non-electrolytes lower the maximum of the electro-capillary curve and in many cases cause a lateral movement of the whole curve.

Frumkin (*Zeit. f. Phys.* XXXV. 792, 1926) considers the effect of replacement of a water molecule at the interface by one of smaller dielectric constant; the electrical work of adsorption is given by

$$\tfrac{1}{2}(c - c')\, V^2,$$

where V is the electrical potential and $c - c'$ the capacity change of the interface when water is replaced by organic molecules. If the molecules adsorbed likewise possess an electric moment there will be an additional term which may be written

$$c' V V_N,$$

where V_N is the potential difference due to the dipoles when the mercury surface is uncharged and completely covered with adsorbed molecules. The electrical work of adsorption W at the potential V is accordingly

$$W = \tfrac{1}{2}(c - c')\, V^2 + c' V_N V.$$

This change in the work of adsorption due to the potential V may by Boltzmann's distribution principle be considered as causing a dilution of the original solution in the ratio $e^{\frac{W}{RT}}$. Such a dilution causes an alteration in the surface tension and the relation between this dilution and the surface tension can be calculated with the aid of one of the appropriate equations of state (Ch. II, p. 67).

Frumkin obtains a fair agreement between the calculated and observed values in the case of amyl alcohol in normal sodium chloride as electrolyte in a capillary electrometer. If the potential difference between the mercury and water be large then the organic molecules of lower dielectric constant are forced out of the double layer and the form of the electro-capillary curves over this region is thus unaltered. There is in many cases a close parallelism between the adsorption of these non-electrolytes at an electrolyte mercury and an electrolyte air interface (see p. 343). Frumkin (*loc. cit.*) gives the following values:

Substance	Γ_∞ water/air grm. mols per sq. cm. × 10^{10}	Γ_∞ water/mercury grm. mols per sq. cm. × 10^{10}
Tertiary amyl alcohol	4·4	4·3
Normal caproic acid	5·38	5·6
p-Cresol	5·8	8·2
o-Cresol	4·8	5·8
Pyrocatechin ...	1·8	4·0
Pyrogallol	2·3	2·7

In the case of the phenols it is clear that the orientation of these molecules at the two interfaces cannot be identical, and the peculiarities in the adhesion of organic substances containing halogens and sulphur to the mercury surface have already been noted. Frumkin finds for example that β-iodo-propionic acid is some thirty-six times more strongly adsorbed at a mercury-water interface than the β-chlor acid, this large increase in adsorbability not being observed at a water-air interface.

In the expression developed above the assumption is made that the electric moment of the adsorbed molecule remains constant during adsorption. This we have seen is not necessarily the case at a solid gas interface and Butler (*Proc. Roy. Soc.* A, CXXII. 399, 1929) has calculated in the following manner the work of adsorption allowing for the induced polarisation of the molecule as it is brought near the charged surface.

The work done in moving an element of dielectric of volume δv from a region of zero field to one where it is E is given by

$$W = \delta v \int P \delta E,$$

where P is the polarisation per unit volume corresponding to a field strength E. In moderate fields, $P = \alpha E$ and $W = \delta v \tfrac{1}{2} \alpha E^2$. If A be the solvent and B the solute present in relatively small concentrations, on moving a molecule of B of volume δv_B from a region I to a region II it displaces an equal volume of A in the opposite direction and the work done is given by

$$W = \tfrac{1}{2} (\alpha_A - \alpha_B) E^2 \delta v_B.$$

If in addition to this induced polarity the molecules possess a permanent electric moment P per unit volume there will be an additional amount of work equal to $(P_A - P_B) E \delta v_B$ and the total electrical work is accordingly

$$W = [\tfrac{1}{2} (\alpha_A - \alpha_B) E^2 + (P_A - P_B) E] \delta v_B.$$

If Γ_0 be the excess concentration of B when $V = 0$ and Γ the concentration at the potential V then applying the Boltzmann distribution principle

$$\Gamma = \Gamma_0 \, e^{-(aV^2 + bV)},$$

where

$$E = \kappa V \quad \text{and} \quad a = \frac{\tfrac{1}{2} (\alpha_A - \alpha_B) \kappa^2 \delta v_B}{kT} \quad \text{and} \quad b = \frac{(P_A - P_B) \kappa \, \delta v_B}{kT},$$

a form somewhat similar to that of Frumkin.

From this it follows that $\Delta\sigma$ the depression of the surface tension at the potential V is given by

$$\Delta\sigma = \Delta\sigma_0 \, e^{-(aV^2 + bV)},$$

where $\Delta\sigma_0$ is the depression where $V = 0$.

Butler examines Gouy's electro-capillary curves for a number of electrolytes containing non-electrolytes and is able to account quantitatively for the main features of the curves. He considers that the maximum adsorption of the organic molecules occurs at the point at which the effect of the electrical attraction of the surface for the dipoles is just balanced by the repulsive effects of the induced dipoles.

6. The structure of the boundary layer.

Neither Gibbs' equation nor that of Lippmann gives us any information as to the structure of the boundary layer. Helmholtz, as we saw, considered it to consist of a charge on the metal surface separated from a layer of ions of opposite sign situated at a small distance from the surface. He did not, however, enquire how these ions were kept separate from the surface or whether the charges should be considered as separated by a dielectric medium.

From Helmholtz's equation it is possible to calculate the equivalent thickness of the double layer δ, as well as the electric moment μ, i.e. the distance to which a proton and an electron must be separated, *in vacuo*, to give the same electric moment. From a knowledge of V and Γ we are in a position to calculate the electric moment of each adsorbed molecule; a few of these are given in the following table:

Substance	Interface	Double layer thickness per molecule in Å. for $\Gamma = 1 \times 10^{-10}$ grm. mols per sq. cm.	Double layer thickness per molecule in Å. for $\Gamma = 2 \times 10^{-10}$ grm. mols per sq. cm.
n-Butyric acid ...	Water-air	0·06	0·06
Tertiary amyl alcohol	Water-mercury	0·05	0·05
Cane sugar	,,	very small	very small
Potassium iodide ...	,,	0·24	[0·15]
Mercurous sulphate	Dilute acid-mercury	0·23	0·20
Sodium oleate ...	Borate buffer—oleic acid	[0·2]	[0·15]

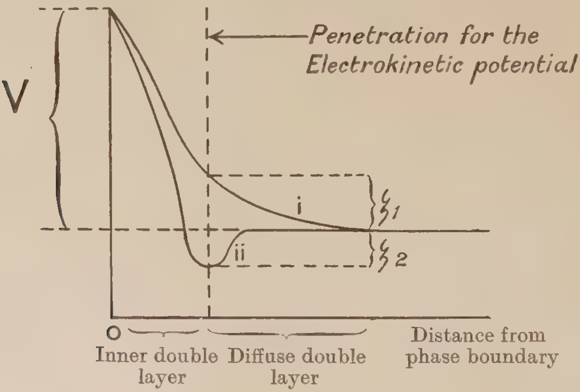
Whilst the electric moment so calculated is in reality not an absolute value, since it is actually only the alteration in electric moment of the surface produced by substituting the adsorbed solute molecules for solvent molecules, yet it is clear that the ionisable substances possess large values which vary within wide limits as the surface concentration is altered. We must conclude that since the apparent molecular electric moment varies with the concentration that Helmholtz's conception of a rigid double layer must be replaced by some species of boundary layer which varies in structure with the surface concentration. Gouy (*loc. cit.*) was the first to consider in detail the mechanism by which the ions are kept away from the charged surface. He put forward the view that the finite value of δ is due to their thermal agitation. On this idea a solution say of $\frac{M}{10}$ NaCl is of uniform concentration at some distance from the electrode but if the latter be charged negatively the concentration of the cations increases as its surface is approached and that of the anions decreases; the osmotic forces which tend to re-establish a uniform concentration being balanced at each point by the electric force due to the potential gradient. On the assumption that the ions were point charges in ideal solution of dielectric constant 80, Gouy calculated the distance of the "centre of gravity" of the volume charge caused by the excess of cations and deficit of anions from the electrode surface as a function of the concentration of the solution and the surface charge ϵ. The following are the values calculated for a decinormal solution of a uniunivalent salt together with the observed values for sodium chloride.

ϵ	Distance of C.G. in cms. $\times 10^{-8}$	δ in cms. $\times 10^{-11}$	δ observed cms. $\times 10^{-11}$
0·0	9·6	100	350 to 490
0·0019	9·6	120	
0·017	9·1	114	
0·33	7·5	94	
0·89	5·4	68	
1·84	3·5	44	
2·60	3·1	39	

The discrepancy between observed and calculated values is considerable. Furthermore, on Gouy's theory of a "diffuse" boundary layer δ should vary inversely as the square root of the concentration: actually it varies very little either with ϵ or the concentration.

Chapman (*Phil. Mag.* XXV. 470, 1913) on the assumption of the applicability of the gas laws and the Boltzmann distribution equation to the ionic atmosphere has calculated the distribution of the ions in the electric field but the expression obtained does not agree well with the experimental results. Stern (*Zeit. Elektrochem.* XXX. 508, 1924) combines the Helmholtz double layer with the diffuse layer of Gouy. According to this view the charge on the metal resides on the surface; the charge in the solution partly as a parallel layer of charge at a distance of the mean ionic radius and partly as a diffuse layer which extends some distance into the solution.

The boundary layer structure is thus complex consisting in general of two parts, an inner condenser-like double layer and an outer or diffuse layer. It is probable that the sheets of the inner layer are separated by but one layer of water molecules possessing a dielectric constant of about 7, the diffuse layer stretching a not inconsiderable distance into the aqueous phase. It is clear that the potential gradient giving rise to V the interface potential is not uniform but is probably steeper over the inner double layer and falling off more gently across the outer or diffuse layer. In some cases at least it is possible that a twofold ionic stratification may exist before the outer layer is reached, the potential distance curve thus presenting a point of inflexion as indicated by (ii) in the following diagram.


V
Penetration for the Electrokinetic potential
i
ζ_1
ii
ζ_2
O
Inner double layer
Diffuse double layer
Distance from phase boundary

In addition to the interphase potential difference V there exists another potential difference of fundamental importance in the theory of the electrical properties of colloids, namely the electrokinetic potential, ζ, of Freundlich. As we shall note in subsequent sections the electrokinetic potential is a calculated value based upon certain assumptions for the potential difference between the aqueous bulk phase and some apparently immobile part of the boundary layer at the interface. Thus ζ represents a part of V but there is no method yet available for determining how far we must penetrate into the boundary layer before the potential has risen to the value of the electrokinetic potential ζ, whether in fact ζ represents part of, all or more than the diffuse boundary layer. It is clear from the above diagram that ζ bears no relation to V; the former may be in fact either of the same or opposite sign, a conclusion experimentally verified by Freundlich and Rona.

7. Gas films at metal electrolyte interfaces.

The electrode potential of both polarised cathodes and anodes varies with the current density giving rise to the phenomena of hydrogen and oxygen over-potentials. At small current densities when the formation of bubbles of gas does not affect the surface area the relationship between the potential changes and the discharge of definite quantities of electricity can be examined. The effects of gas films formed in this manner have been examined by Bowden and Rideal and by Bowden (*Proc. Roy. Soc.* A, cxx. 60, 1928; cxxv. 446, 1929). Studying the cathodic mechanism in oxygen-free electrolytes it was found that the potential change was a linear function of the quantity of electricity passed, viz. 100 millivolts per 6×10^{-7} coulombs per accessible sq. cm. This linear relationship was found to be independent of the nature of the underlying metal, thus furnishing a method for the evaluation of the accessible surfaces of metals (see Ch. v, p. 176). The total amount of electricity that must be passed to change the potential of a platinum electrode from that of the reversible hydrogen to that of the reversible oxygen electrode was found to be $9 \cdot 10^{-4}$ coulombs per accessible sq. cm. The number of hydrogen atoms on a platinum surface packed on or between the underlying platinum atoms is *ca.* $1{\cdot}6 \cdot 10^{15}$ per accessible sq. cm. Thus the amount of electricity required to remove $1{\cdot}6 \cdot 10^{15}$ hydrogen atoms in the form of ions and to deposit the equivalent number of divalent oxygen atoms is $3 \times 2{\cdot}7 \cdot 10^{-4}$ or $8{\cdot}1 \cdot 10^{-4}$ coulombs, a value close to that obtained experimentally. Thus the change from the hydrogen to the oxygen potential involves the removal of a monatomic film of hydrogen and its replacement by one of oxygen and since the curve between these two points is linear in form the transformation is a gradual one.

To establish the oxygen over-potential it was found that to raise the potential by 100 millivolts $11 \,.\, 10^{-6}$ coulombs per accessible sq. cm. had to be passed, a value to be compared with $6 \,.\, 10^{-7}$ coulombs for hydrogen. If the potential difference across the interface be regarded from the point of view of Helmholtz as due to a number of electric doublets each possessing a finite electric moment then the potential change is given by

$$\Delta V = 4\pi\mu\Delta n.$$

Inserting the above values we find that μ for the hydrogen is $7{\cdot}2 \,.\, 10^{-18}$ E.S.U. and for the oxygen $7{\cdot}8 \,.\, 10^{-19}$ E.S.U.

It might be suggested that a hydrogen doublet on the surface of a metal resulting from the discharge of a hydrogen ion is formed by the electrostatic attraction of a hydrogen ion from the solution to the proximity of the discharged atom which, possessing an electron affinity on being attached to the underlying metal, behaves as a negative ion (cf. Heyrovsky, *Rec. Trav. Chim.* XLIV. 499, 1925; XLVI. 582, 1927).

Since the doublets are of the order of molecular dimensions a change of 100 millivolts is equivalent to a change in the electric field strength of the double layer of 10^6 to 10^7 volts per cm., strong enough to produce deformation of the doublets, and thus alter their length of life on the surface of the metal. The rate of decay or rate of evaporation of the electro-deposited hydrogen doublets was also examined by Bowden. If the energy necessary for a dipole to evaporate or escape be W, this energy can be supplied both by thermal agitation and by increasing the potential across the double layer and thus causing further deformation of the doublets; we can thus write

$$W = w + \alpha V.$$

The fraction of dipoles possessing this energy will be

$$N = N_0 e^{-\left(\frac{w+\alpha V}{RT}\right)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(1),$$

or on differentiating with respect to V we obtain

$$\frac{\partial \log N}{\partial V} = 2{\cdot}3\,\frac{\partial \log i}{\partial V} = \frac{\alpha}{RT} \quad \ldots\ldots\ldots\ldots\ldots(2).$$

From a plot of the $\log i$, V curves for the rate of liberation of hydrogen from different surfaces it was found that for hydrogen on a variety of metallic surfaces and for oxygen on platinum the value of α was 0·5 in agreement with the experiments of Tafel (*Zeit. physikal. Chem.* L. 641, 1908). On contaminated surfaces α for hydrogen falls to a value as low as 0·2 on an old mercury surface. The expressions connecting the rate of evaporation of the doublets are obtained from (1) in the form

$$\left(\frac{\partial \log N}{\partial T}\right)_V = 2{\cdot}3\,\frac{\partial \log i}{\partial T} = \frac{w+\alpha V}{RT^2}\;\ldots\ldots\ldots\ldots(3),$$

and $$\left(\frac{\partial V}{\partial T}\right)_i = \frac{w+\alpha V}{\alpha T} \quad\text{or}\quad w+\alpha V = \alpha T\frac{dV}{dT}\;\ldots\ldots(4).$$

From these equations it is possible to evaluate $w+\alpha V$, the energy of activation which must be supplied to a gas dipole in order that it may evaporate from the surface.

In the case of liberation of hydrogen at a mercury surface $\frac{\partial \log i}{\partial T}$ at 36° C. at the potential of $-$ 1·0 volt on the saturated calomel scale was found to be 0·023, whence $w+\alpha V = 0{\cdot}43$ volts. At a current density of 1 . 10^{-5} amps per cm.^{2} and the potential being the same as before $\frac{\partial V}{\partial T}$, was found to be 0·0026 volts/degree, giving a value of $w+\alpha V = 0{\cdot}41$ volts, a value in good agreement with that obtained from the variation in the current with the temperature at constant voltages.

For oxygen on platinum values of 0·47 and 0·44 volts were found by the two methods.

We may note that these measurements were taken at a potential difference between mercury and the electrolyte of $-$ 1·0 volts on the saturated calomel scale, or $-$ 0·47 volts on the absolute scale. Since $W = w+\alpha V = 0{\cdot}42$ volts, we obtain

$$w = 0{\cdot}42 + 0{\cdot}5 \times 0{\cdot}47 = 0{\cdot}65 \text{ volts,}$$

equivalent to an energy of activation of 15,000 calories per grm. mol. For oxygen on platinum the energy of activation is found to be 23,000 calories per grm. mol and for hydrogen on fresh platinum a value as low as 7000 cals. per grm. mol was found rising to 9000 cals. with increasing age of the surface.

Bowden likewise noted that the discharge of hydrogen doublets could be photo-accelerated.

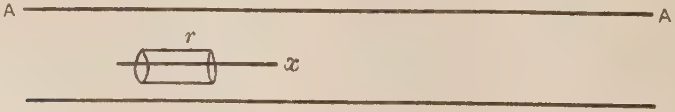
8. Motion due to the electrokinetic potential.

If charcoal be immersed in dilute hydrochloric acid the hydrogen ions are adsorbed more readily than the chlorine ions. Owing however to the electrostatic attraction between the ions of opposite sign, a diminution in the equilibrium surface concentration of the hydrogen ions, and an increase in excess of the equilibrium concentration of the chlorine ions occur. The system as a whole is electrically neutral, but between the charcoal and the solution a difference of potential will be created, a measure of the excess of hydrogen ions over chlorine ions adsorbed. The solid will thus acquire a charge relative to the liquid, and on impressing an E.M.F. on the system, the liquid will move past the solid, if this be kept stationary, a phenomenon termed electric endosmose; whilst if the solid be present as small particles these will move through the solution to one or other of the electrodes, a motion to which the term electric cataphoresis has been applied.

9. Electric endosmose.

In 1808 Reuss (*Mém. de la Soc. de Moscou*, II. 327, 1809) observed that on passage of an electric current through a cell containing an earthenware diaphragm the electrolyte was transferred from the anode to the cathode compartment. Porret (*Pogg. Ann.* LXVI. 272, 1816; LXXVIII. 618, 1828) observed a similar phenomenon with a sand diaphragm. Wiedemann (*ibid.* LXXXVII. 321, 1852; XCIX. 177, 1856) was, however, the first to conduct a series of systematic experiments on the subject. The theory that any electric "double layer" was the cause of the phenomenon was first suggested by Quincke (*ibid.* CXIII. 513, 1861) and developed by Helmholtz (*Ann. de Phys. Chim.* VII. 337, 1879; *Ges. Abhandlungen*, I. 855, 1882).

The relationship between the quantity of liquid transported and the current has been developed in the following manner by Porter (*Trans. Farad. Soc.* XLVIII. 133, 1921).



Consider the stream line flow of liquid through a narrow capillary tube AA of cross-sectional area A to which a longitudinal voltage $V_1 - V_2$ is applied so as to be uniform across the cross-section. If there is a charge q anywhere in the liquid the force acting on the charge is $-q\frac{dV}{dx}$.

We select a cylinder of unit length and radius r enclosing the charge q, then the total normal induction over the cylinder is, by Gauss's theorem, $\frac{4\pi q}{K}$, where K is the specific inductive capacity of the liquid. The curved area of the cylinder is $2\pi r$ and the electric force outwards from the curved surface is

$$-\frac{dV}{dr},$$

hence
$$\frac{4\pi q}{K} = 2\pi r\left(-\frac{dV}{dr}\right).$$

When a steady flow u is set up the longitudinal force on the charge balances the frictional force against the curved area or

$$-q\frac{dV}{dx} = -2\pi r\eta\frac{du}{dr},$$

where η is the viscosity.

Eliminating q we obtain

$$K\frac{dV}{dr} = \frac{4\pi\eta\frac{du}{dr}}{-\frac{dV}{dx}}.$$

The electric current C is by Ohm's law equal to

$$-\frac{dV}{dx}\frac{A}{R},$$

where R is the specific resistance of the liquid.

Hence
$$\frac{dV}{dr} = \frac{4\pi\eta A}{KRC}\frac{du}{dr}.$$

This equation is independent of the particular distribution of the electric charge across the cross-section.

If V_m and u_m are the potential and velocity at a point on the tube axis and V_w and zero the corresponding values for the tube wall

$$V_m - V_w = \zeta = \frac{4\pi\eta A}{KCR}u_m.$$

If the charges in the liquid forming part of the double layer are in close proximity to the tube wall there will be no charge in the bulk of the liquid, i.e. $q = 0$ or $\frac{du}{dr} = 0$; thus the liquid will move through the tube with a uniform velocity equal to u_m.

The total liquid flow will consequently be $u_m A = U$ say.

Hence
$$U = \frac{KRC}{4\pi\eta}(V - V_w) = \frac{KRC}{4\pi\eta} \cdot \zeta,$$

where ζ is the transverse voltage or electrokinetic potential

$$= \frac{KA}{4\pi\eta} \times \text{longitudinal voltage} \times \text{transverse voltage}.$$

The transverse voltage ζ is the drop of potential across the double layer and is of the order of 0·01 to 0·05 volt. It will be noted that the amount of liquid transported is dependent on the nature of the liquid and on the current and is independent of the diameters or lengths of the tubes of the diaphragm. Somewhat divergent views are held as to the actual thickness of the double layer (Lamb, *Phil. Mag.* XXV. 52, 1888), a point which we have already referred to.

In a similar manner the actual hydrostatic pressure difference P produced by electric endosmose can be calculated, with the following result:
$$P = \frac{2\zeta(V_1 - V_2)K}{A}.$$

On forcing a liquid through a diaphragm, diaphragm currents are set up, a phenomenon noted by Wiedemann and Quincke and one fully accounted for on the hypothesis of the existence of an electrical double layer between the diaphragm material and the liquid.

As has been indicated above the formation of the electric double layer of potential ζ is attributed to the selective or preferential adsorption of one ion. The influence of the nature of the electrolyte on both the magnitude and sign of the electric double layer as indicated by electric endosmose experiments was first studied in detail by Perrin (*J. Chim. Phys.* II. 601, 1904; III. 50, 1905; see also Hittorf, *Zeit. physikal. Chem.* XXXIX. 613, 1902; XLIII. 239, 1903; Baudouin, *C.R.* CXXXVIII. 898, 1904;

Ascoli, *ibid.* CXXXVII. 1253, 1903; Guillaume, *ibid.* CXLVII. 53, 1908; Elissafoff, *Zeit. physical. Chem.* LXXIX. 385, 1912; Bethe and Toropoff, *ibid.* LXXXVIII. 686, 1914; LXXXIX. 597, 1915; Glixelli, *Bull. de l'Acad. des Sciences de Cracovie*, A, 102, 1917; Gyemant, *Koll. Zeit.* XXVIII. 103, 1921). The general conclusions in regard to the influence of various electrolytes on electric endosmose may be briefly summarised as follows:

In accordance with theoretical expectations only strongly ionising solvents exhibit marked endosmose, e.g. chloroform and benzene are practically inert whilst nitrobenzene, the alcohols and water exhibit the phenomenon to a marked extent. Of the ions adsorbed by materials constituting the diaphragms, as in the case of direct adsorption, the hydrogen and hydroxyl ions have the greatest influence. In acid solutions most diaphragm materials acquire a positive charge relative to the liquid which moves to the anode, in alkaline solutions hydroxyl ions are adsorbed and the liquid moves to the cathode being positive relative to the negatively charged diaphragm.

If the solid diaphragm material adsorbs both hydrogen and hydroxyl ions it is evident that electric endosmose will cease when equal ionic adsorption has taken place, the double layer potential or electrokinetic potential being at this point zero and the diaphragm is at the isoelectric point.

No substance examined appears to have an isoelectric point identical with pure water $P_H = 7$ where the solution contains identical concentrations of both hydrogen and hydroxyl ions and in general most materials adsorb hydrogen ions more readily than hydroxyl ions.

In the tables overleaf are given the concentrations of solutions necessary to change the sign of a few typical diaphragms and the relative rates of electric endosmose through diaphragms of identical thickness.

Agar-agar, collodion and cellulose appear always negative except in strongly acid solutions. Various relatively insoluble bases and acids have been employed as diaphragm materials by Glixelli (*Bull. de l'Acad. des Sc. de Cracovie*, 1917) and Gyemant (*Koll. Zeit.* XXVIII. 103, 1921), and as anticipated the isoelectric points of the basic diaphragms are found in weakly alkaline

Diaphragm material	Solution	Diaphragm charge	Relative rate of electric endosmose
AgCl	$\frac{N}{500}$ HCl	+	3
	$\frac{N}{500}$ NaOH	−	5
$CrCl_3$	$\frac{N}{1000}$ HCl	+	9·5
	$\frac{N}{500}$ KOH	−	8·5
Blood charcoal	$\frac{N}{100}$ HCl	+	2·6
	$\frac{N}{1000}$ HCl	+	1·4
	$\frac{N}{20,000}$ HCl	+	0·7
	$\frac{N}{50,000}$ HCl	−	0·4
Gelatine	$\frac{N}{50}$ HCl	+	2·2
	$\frac{N}{100}$ NaOH	−	3·5
Kaolin	$\frac{N}{10}$ HCl	0	0
	$\frac{N}{100}$ HCl	−	0·6
	$\frac{N}{1000}$ HCl	−	6·1
	$\frac{N}{1000}$ NaOH	−	18·2

solutions, of the acid diaphragms in acid solutions, as indicated by the data given on p. 327.

In the case of adsorption on charcoal it is found that the organic ions are more strongly adsorbed than either hydrogen or hydroxyl. Whilst the other cations and anions are adsorbed to varying extents, the position of the ion in the electropositive series, the mobility and the valency appear to be the dominating influences.

Freundlich (p. 355) gives the following values calculated from endosmotic rate experiments for the concentrations of various

	Solution	Diaphragm charge	Relative rate of endosmose
Basic diaphragms:			
Fe_2O_3	H_2O	+	10·50
	0·001*N* HCl	+	67·00
	0·0001*N* $AlCl_3$	+	103·00
	0·001*N* NaOH	–	16·00
ZnO	H_2O	+	0·31
	0·0002*N* NaOH	+	0·22
	0·0003*N* NaOH	–	0·16
	0·0004*N* NaOH	–	0·24
$Mg(OH)_2$ ...	H_2O	+	0·64
	0·0006*N* NaOH	+	0·05
	0·02*N* NaOH	–	0·90
Acid diaphragms:			
Silica	H_2O	–	0·63
	0·03*N* HNO_3	–	0·33
	0·47*N* HNO_3	–	0·12
Tungstic acid	H_2O	–	2·66
	0·045*N* HCl	–	1·12
	0·207*N* HCl	–	0·28
	0·8*N* HCl	–	0·00

electrolytes necessary to produce an identical diminution in the double layer potential or ζ values.

Electrolyte	Concentration in millimols per litre	
	Oil-water interfacial potential reduced from 0·046 to 0·037 volt	Glass-water interfacial potential reduced from 0·089 to 0·039 volt
KCl	24	25
$BaCl_2$	0·450	0·870
$AlCl_3$	0·010	0·020
$ThCl_4$	0·005	0·015

In the case of acids the hydrogen ion is more strongly adsorbed than the anion, giving the diaphragm a positive charge. If however the acid containing a feebly adsorbed anion, e.g. chloride ion, be replaced by one containing a more strongly adsorbable anion, e.g. SO_4'', the double layer potential due to the difference in electrostatic charge will be diminished and the velocity of electric endosmose reduced as is shown by the following data obtained by Perrin (*loc. cit.*):

Diaphragm	Solution	Diaphragm charge	Relative rate of electric endosmose
Al_2O_3 ...	$\frac{N}{1000}$ HNO_3	+	10·0
	$\frac{N}{1000}$ HCl	+	10·0
	$\frac{N}{1000}$ H_2SO_4	+	1·5

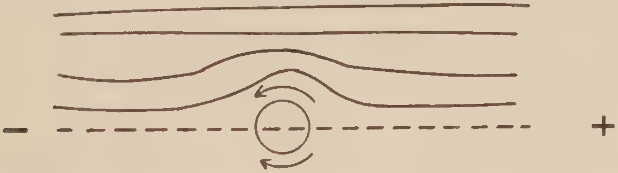
In some cases with a strongly adsorbed anion actual reversal of sign may take place, e.g.

Diaphragm	Solution	Diaphragm charge	Relative rate of electric endosmose
$CrCl_3$ ...	Dilute acid	+	5·9
	+ $\frac{N}{1000}$ $K_3Fe(CN)_6$	+	0·2
	+ $\frac{N}{50}$ $K_3Fe(CN)_6$	−	2·0
Mn_2O_3 ...	Dilute alkali	−	4·0
	+ $\frac{N}{500}$ $Ba(NO_3)_2$	+	1·8
	$\frac{N}{50}$ HCl	+	3·8
Naphthalene	$\frac{N}{100}$ HCl	+	3·9
	$\frac{N}{1000}$ HCl	+	2·8
	$\frac{N}{5000}$ HCl	+	0·3
	$\frac{N}{5000}$ KOH	−	2·9
	$\frac{N}{1000}$ KOH	−	6·0
	$\frac{N}{50}$ KOH	−	6·0

The attainment of a definite maximum for this transverse potential can readily be demonstrated in that a maximum rate of endosmotic flow is obtained on the addition of electrolyte in increasing concentrations, a phenomenon well marked in the case of naphthalene.

10. Electric cataphoresis.

Preliminary data on cataphoresis or the rate of migration of a charged particle through a solution under the influence of an applied potential difference were made by Quincke (*loc. cit.*) and Linder and Picton (*J.C.S.* LXI. 67, 1887), whilst accurate measurements have been made by Burton (*Phil. Mag.* 6, XI. 440, 1906; XII. 474, 1906), Ellis (*Zeit. physikal. Chem.* LXXVIII. 321, 1912), Powis (*ibid.* LXXXIX. 91, 1915), Svedberg (*Koll. Zeit.* XXIV. 156, 1919), Cotton and Mouton (*Les Ultramicroscopes*, ch. VII). The following development is given by Porter (*loc. cit.*), for the influence of the double layer potential ζ and the physical constants on the velocity of migration.



A particle is imagined to move with a uniform velocity v through a liquid under the influence of an impressed electromotive force.

If an equal opposite velocity to that of the particle be impressed on the whole system the particle will be at rest whilst the liquid at a great distance will have a uniform motion v. Let the gradient of potential driving the current also be uniform at a great distance and equal to G, both v and G being parallel to x.

At a great distance the potential will be given by $V = -Gx$, whereas near the particle additional terms will enter, due to the disturbance introduced by the presence of the particle. When the motion is slow it is irrotational and can be derived from differentiation of a potential function ϕ; at a great distance $\phi = -Vx$.

Assuming a slip (Lamb, *loc. cit.*) at the surface of the particle $u_0 = -\frac{d\phi}{dS}$; the corresponding force due to friction on unit area is $-\beta\frac{d\phi}{dS}$, where β is the coefficient of friction.

The force on the charge of the element is $-q\frac{dV}{dS}$ and for steady motion

$$\beta\frac{d\phi}{dS} = -q\frac{dV}{dS}.$$

This condition is satisfied if we take $\frac{V}{\phi} = \frac{\beta}{q}$ everywhere.

Hence $$\frac{G}{v} = \frac{\beta}{q} \text{ also.}$$

But v is equal and opposite to the actual velocity of the particle and G is the gradient of potential $-\frac{dV}{dx}$ in the undisturbed part of the field. Hence if c be the current per unit area in this part we obtain

$$c = \frac{1}{R}\frac{dV}{dx} = \frac{G}{R},$$

and therefore $$-v = \frac{qRc}{\beta}.$$

The radial voltage at the particle ζ is q/capacity per unit area $= q\frac{4\pi\delta}{K}$, where δ is the double layer thickness and q the charge per unit area of the particle.

Also as before

$$\beta u_0 = \eta\frac{du}{dr} = \eta\frac{u_0}{\delta},$$

whence $$-v = \frac{KRC}{4\pi\eta}\zeta,$$

identical with the endosmotic equation but with reversed sign.

On applying this equation to a small spherical particle of olive oil in an emulsion, McLewis (*loc. cit.*; *Zeit. Koll.* IV. 211, 1909) found $\zeta = 0{\cdot}05$ volt.

Now $$\zeta = \frac{q4\pi\delta}{K}.$$

If r be the radius of the particle and ϵ the total charge then

$$\epsilon = 4\pi r^2 q \text{ or } q = \frac{\epsilon}{4\pi r^2} \text{ and } \zeta = \frac{4\pi\delta\epsilon}{4\pi r^2 K} = \frac{\delta\epsilon}{Kr^2},$$

the radius of the particle was found to be $4 \,.\, 10^{-5}$ cms., δ was assumed equal to $5 \,.\, 10^{-5}$ cms., hence the total charge was $4 \,.\, 10^{-4}$ E.S.U.

For colloidal platinum a somewhat smaller value was obtained for the total charge, viz. $8 \,.\, 10^{-5}$ E.S.U.

It will be noted that in the derivation of the transverse potential difference ζ the product ηv should be constant for the same system under uniform conditions. A change in η can be produced most conveniently by alteration of the temperature. Burton (*Physical Properties of Colloidal Solutions*, p. 145) gives the following data for colloidal silver solutions in support of the validity of the equation.

° C.	$v \times 10^5$	$\eta \times 10^3$	$\eta v \times 10^7$
3	15·1	16·21	24·5
9·9	18·6	13·30	24·7
11	19·6	12·82	25·1
21	25·5	9·92	25·0
31	30·1	7·97	24·0
40·5	37·2	6·577	24·5

Burton has likewise investigated the effect of the medium on the mobility and on the transverse potential fall, since these should be dependent both on the viscosity and on the specific inductive capacity; as typical of the results obtained the following may be cited:

Suspension		Water	Methyl alcohol	Ethyl alcohol	Ethyl malonate
	S.I.C.	80	33	25·8	10·6
Platinum	$v \times 10^5$	20·3	—	—	2·3
	ζ	– 0·031	—	—	– 0·054
Gold ...	$v \times 10^5$	21·6	—	—	1·7
	ζ	– 0·033	—	—	– 0·033
Lead ...	$v \times 10^5$	12·0	22·0	4·5	—
	ζ	+ 0·018	+ 0·044	+ 0·023	—

In the following table are inserted a few typical values for the mobility in cms. per sec. per volt per cm. (v) and the transverse potential fall ζ for various particles in aqueous solution.

Substance	$v \times 10^5$	ζ
Hydrocarbon oil...	− 43·0	− 0·060
Aniline	− 31·1	− 0·043
Chloroform ...	− 10·0	− 0·014
Lycopodium ...	− 25·0	− 0·035
Prussian blue ...	− 40·0	− 0·056
Gold	− 21·6	− 0·030
Silver	− 23·6	− 0·033
Globulin in NaOH	+ 7·7	+ 0·100
„ H_2SO_4	− 18·5	− 0·026
Lead	+ 12·0	+ 0·017
Arsenious sulphide	− 22·0	− 0·031

11. Electrification at gas-liquid interfaces.

In the first chapter we noted that according to Sir W. Hardy the molecular electric field around complex molecules was not symmetrical and, as a result of this asymmetry, molecular orientation at the gas-liquid interface was obtained. Langmuir identified the asymmetrical parts of the molecular field with specific chemical groups in the molecule, the "polar" heads possessing large fields. The constitutive character of the molecular electric moment determined from dielectric constant data demonstrated especially by Debye (*Polar Molecules*) confirms this conclusion. The existence of electrical forces at gas-liquid interfaces is shown in the ballo-electric phenomena investigated by Lenard (*Wied. Ann.* XLVI. 584, 1892) who found that a stream of atomised water when allowed to impinge on an insulated metal plate imparted a charge to the plate, leaving a negative charge in the surrounding vapour. More precise evidence in this direction was presented by McTaggart (*Phil. Mag.* XXVII. 297, 1914; XXVIII. 367, 1914) and Alty (*Proc. Roy. Soc.* A, CVI. 316, 1924; CX. 178, 1926; CXII. 235, 1926; CXXII. 623, 1929) who showed that gas bubbles underwent electric cataphoresis in water usually towards the anode, thus proving the existence of an electrokinetic potential at the gas-water interface. In pure water the bubble is very near the isoelectric point but in the presence of small quantities of salts the bubble surface becomes negatively charged, leaving a positive charge in the mobile double layer in the water, indicating that even in cases of negative adsorption (Ch. II) there is still a selective adsorption of anions at the air-liquid interface. The addition of acids as well as of multivalent cations such as lanthanum and thorium lowers and finally reverses the electrokinetic potential. It was noted that aliphatic alcohols, strongly adsorbed at the air-water interface, diminished the rate of migration considerably.

McTaggart observed a curious effect when a bubble underwent cataphoresis in water not saturated with gas. If the bubble was negatively charged it moved more slowly as it became smaller, passed through the isoelectric point and finally reversed its sign. A trace of a capillary active substance present in the water, the surface concentration of which becomes greater as the bubble size diminishes, might effect this result.

McBain and Peaker (*Proc. Roy. Soc.* A, CXXV. 394, 1929) have shown that the conductivity of the water in contact with a film of stearic acid on the surface is greater than the conductivity of the bulk solution; it is however impossible to evaluate the electrokinetic potential from such data alone.

In addition to the electrokinetic potential at air-liquid interfaces there exists a phase boundary potential and valuable information on molecular orientation and structure has been obtained by observing the change in phase boundary potentials on adding capillary active substances to the aqueous phase. The method developed by Bichat and Blondlot (*J. de Physique*, (2) II. 548, 1883) and Kenrick (*Zeit. physikal. Chem.* XIX. 625, 1896) consisted in measuring the E.M.F. of a cell of the type

$$\mathrm{Hg\;Hg_2Cl_2}\;n\text{-}\mathrm{KCl}\;\Big|\;\underset{A}{\text{Solution}}\;\Big|\;\underset{\text{gap}}{\text{Air}}\;\Big|\;\underset{B}{\text{Solution}}\;\Big|\;n\text{-}\mathrm{KCl\;Hg_2Cl_2\;Hg}$$

but the experimental technique was greatly improved by Guyot (*C.R.* CLIX. 307, 1914; *Ann. d. Phys.* X. 2501, 1924) and by Frumkin (*Zeit. physikal. Chem.* CIX. 34, 1924; CXI. 190, 1924; CXV. 190, 485, 1925).

The earlier experimental methods consisted essentially in measuring the difference of potential between a jet of liquid flowing down the axis of a vertical tube and a liquid film flowing down the inner wall of the tube. The natural ionisation of the air was relied upon to impart sufficient conductivity to the air gap so as to permit of the measurement by means of a sensitive quadrant electrometer of the potential differences between calomel electrodes connected to the two liquids. In Guyot's and Frumkin's experiments the flowing jet of reference liquid was replaced by a small platinum wire, coated with a radioactive salt such as the oxide of ionium, polonium or even uranium. This electrode was separated by a small air gap from the liquid contained in a well-insulated glass trough. The other electrode consisted of a calomel half-cell immersed in the liquid and the potential difference established was measured with the aid of a potentiometer and quadrant or Lindemann type electrometer.

The trough is first filled with the reference liquid, $0{\cdot}01N$ H_2SO_4 or $0{\cdot}01N$ HCl being frequently employed, and is then replaced by the solution to be investigated or covered with a unimolecular film from a volatile solvent if non-soluble film forming materials are under examination. The difference of potential obtained $V_f - V_0 = \Delta V$ may be regarded as the modification of electric potential at the interface produced by the adsorbed solute or the film. It clearly gives no definite indication of the absolute potential difference to be expected.

Further if each adsorbed molecule be regarded as contributing an integrated electric moment the value of the vertical component of which is μ, this may be determined from a knowledge of ΔV and the surface concentration n with the aid of the Helmholtz equation

$$\Delta V = 4\pi n\mu \quad \text{.........................(1).}$$

When capillary active soluble substances are employed and due corrections made for any change in potential difference at the calomel solution interface we may combine this equation with that of Gibbs

$$n = -\frac{d\sigma}{d\mu},$$

whence

$$\mu = -\frac{\Delta V d\mu}{4\pi d\sigma} = \frac{\Delta V RT}{4\pi\,(fc)}\frac{dfc}{d\sigma}.$$

The relationship between ΔV and n for a number of capillary active soluble organic substances has been investigated by

Frumkin who showed that to a first approximation at any rate the value of ΔV obtained for a given surface concentration at constant temperature was, in the case of homologous series such as the acids, independent of the chain length; a few data are given in the following table:

Acid	c mols/litre	$RT\Gamma$	ΔV millivolts
n-Butyric	0·758	12·35	349
n-Valeric	0·132	12·45	355
n-Caproic	0·195	12·60	353

From the data it is possible to calculate the value of μ, the vertical component of the integrated resultant electric moment of the double layer brought into existence by the molecule on the surface. For the butyric acid solution above $\Delta V = 349$ millivolts $= 1{\cdot}16 \,.\, 10^{-3}$ E.S.U. and from the value of Γ, $4\pi n$ is found to be $3{\cdot}79 \,.\, 10^{15}$. Whence $\mu = 3{\cdot}05 \,.\, 10^{-19}$ E.S.U. If this effective moment be imagined as caused by a double layer of thickness δ then $\mu = \epsilon\delta$, since $\epsilon = 4{\cdot}77 \,.\, 10^{-10}$. Thus we obtain a value for $\delta = 0{\cdot}06$ Å. in close agreement with the values obtained by Gouy for the double layer thickness of capillary active substances at a water-mercury interface. Performing a similar calculation for alcohol molecules we obtain $\delta = 0{\cdot}048$ Å.

It is important to enquire how far we can identify μ obtained with the aid of the Helmholtz equation from ΔV with the effects due to a discrete molecule.

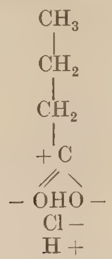
On this point definite experimental evidence is not conclusive; we may note that if the adsorbed molecule behaved as a simple dipole in thermal equilibrium on the surface the value of μ would be dependent on the inclination of the dipole; thus if the real dipole value were $\bar{\mu}$ we would obtain for a molecule with the dipole axis inclined at an angle θ to the normal

$$\Delta V = 4\pi n\bar{\mu} \cos \theta.$$

If this angle of inclination be governed entirely by electrical forces of orientation and the thermal agitation we may replace $\cos\theta$ by the Langevin function $L(x) = \coth x - \frac{1}{x}$, where

$x = \frac{2\pi n\bar{\mu}\epsilon}{kT}$ (Debye, *Handbuch der Radiologie*, p. 617). No investigations have as yet been made on the effects of temperature on surfaces with gaseous films, and in the case of long chain fatty acids there are factors of orientation other than these to be considered.

Again we may note that in the case of a fatty acid molecule floating on the surface of water, say dilute HCl



the effective double layer cannot be regarded as due to a simple dipole. The carboxylic head in the water does not present a simple dipole system and, as we shall see, under the carboxylic head there is a contribution to the electric moment by the ions of the electrolyte adsorbed from the bulk phase. Whilst the contributions from the polar head may be said to be definitely associated with the particular molecule we shall note that the contribution from the ionic layer underneath, at least in solid and liquid films, appears to be constant for a particular state of the film and not dependent on the closeness of packing. The contribution to the total of μ by the portion of the molecule immersed in the water must evidently be very different from that for a polar head *in vacuo* or surrounded by a non-polar environment, although as observed by Frumkin and Williams (*Proc. Nat. Acad. Sci.* xv. 400, 1925) a close parallelism exists between the values of the electric moments determined by Debye's method (*Polar Molecules*) for substances and the smaller values obtained for μ when a molecule is orientated by immersion of its polar head in the surface of water.

Whilst the disposition of electric charge around such molecules is evidently complex it is further complicated by the fact that the molecules may be in close proximity to one another. As the nearness of approach increases two effects may be produced; the molecules may be distorted or inclined at a different angle to the surface which may cause a change in the μ value which is the algebraic sum of the vertical component of the partial moments and there may be effects due to mutual induction causing polarisation and a decrease in the value of μ.

For capillary-active soluble substances in the gaseous or vaporous states where the second factor rather than the first is likely to be more important the evidence for a change in effective moment with change in the surface concentration is inconclusive. Measurements have been made by Frumkin but the experimental errors in measurement at low concentrations as well as errors introduced by utilisation of v. Szyszkowski's equation (p. 57) do not permit of a definite decision. Some of his values are given below.

c mols/litre	ΔV millivolts	$\Gamma \,.\, 10^{10}$	$\frac{\Delta V}{\Gamma} \times 10^{-10}$
	Aniline		
0·0156	12·0	0·30	40
0·0312	29·0	0·84	34
0·0625	97·0	2·5	39
0·25	140·0	5·2	27
	Butyric acid		
0·0061	22·5	0·58	38
0·0153	61·0	1·25	49
0·0306	119·5	2·04	59
0·0574	177·5	2·77	64
0·076	213·0	3·25	66
0·163	285·0	4·14	69
0·758	349·0	5·12	69
	p-Cresol		
0·0006	0·0	0·05	0
0·0012	1·0	0·11	9
0·0023	5·0	0·23	22
0·0047	14·0	0·58	24
0·0094	53·0	1·52	35
0·0187	155·0	3·97	39
0·0375	224·0	5·13	44
0·075	258·0	5·52	47

For more concentrated solutions the proportionality between ΔV and Γ is found to be more exact.

In the case of insoluble substances Frumkin has measured the maximal values of ΔV, i.e. ΔV_∞ obtained on placing an excess of the material on the surface, the condition of the film is then naturally that in equilibrium with the crystal or lens (Ch. IV) and as we have already noted may vary from substance to substance, i.e. the film may be in the vaporous, expanded or condensed state and the equilibrium lens or crystal pressure is greatly affected by the nature of the substrate.

Guyot (*loc. cit.*) determined the potential differences for myristic and palmitic acids at 18° C. and for palmitic acid at 33° C. From the data of Labrouste on the molecular areas he obtained values for $\mu = 2{\cdot}09 \,.\, 10^{-19}$ E.S.U. for both films which must have been in the expanded state, whilst the expansion of Labrouste (see p. 101) was clearly observed. From the potential changes a slightly different value for a condensed film of $\mu = 2{\cdot}24 \,.\, 10^{-19}$ E.S.U. was obtained, he attributed this difference to experimental error.

A careful examination of the ΔV surface concentration curves for myristic and palmitic acids on various solutions in a modified Langmuir trough permitting of compression and expansion of the film has been made by Schulman, who showed that definite changes in the value of μ were associated with changes in state of the film and that there existed under the film an electric double layer formed by the attraction of the ions in solution to the polar surface of the film. In the liquid condensed state, which we have seen is probably the most stable configuration for freely tilting long-chain molecules, myristic acid on $\frac{N}{100}$ HCl possesses at all stages of compression a constant μ value of $1{\cdot}46 \,.\, 10^{-19}$ E.S.U., likewise in the expanded or liquid state the moment is constant and equal to $2{\cdot}70 \,.\, 10^{-19}$ E.S.U., although this value is reduced by $0{\cdot}37 \,.\, 10^{-19}$ E.S.U. per molecule by the double layer of chlorine and hydrogen ions adsorbed beneath the surface. A sharp rise in the value of μ is observed on compression of a solid condensed film and likewise in the transition to the vaporous state there occurs a similar rise. At the moment when vaporisation is just commencing the value of μ rises to $\mu = 3{\cdot}7 \,.\, 10^{-19}$ E.S.U., in good agreement with that calculated from

Frumkin's data, viz. $\mu = 3{\cdot}05 \,.\, 10^{-19}$ E.S.U. for closely packed vaporous films of the lower fatty acids. Indications were obtained of the existence of two types of the vaporous films of long-chain fatty acids consisting of films in which the molecules are inclined and extended horizontally on the surface, the former possessing a large moment.

From the slope of the ΔV, n curves Schulman was able to evaluate the contribution of the ionic double layer underneath the film to the total interphase potential. Some of his results are given in the following table in which μ_x is the true moment of the fatty acid molecule and μ the apparent moment. One notices that the contribution of the double layer may be positive or negative.

Acid	State of film	p_H and nature of buffer		μ_x E.S.U. 10^{19}	μ E.S.U. 10^{19}
Myristic	Expanded	2	$N/100$ HCl	2·70	2·32
Palmitic	Liquid condensed	2	$N/100$ HCl	1·50	2·50
,,	,,	5·6	Citrate	1·46	2·06
,,	,,	6·0	,,	1·46	1·86
,,	,,	6·6	,,	1·46	1·71
,,	,,	—	Water	1·46	1·46
,,	,,	6·4	Borate	1·46	1·30

It is interesting to compare the values of μ obtained in this way, viz. a maximum of $\mu = 3{\cdot}7 \,.\, 10^{-19}$ E.S.U., with those derived by other means. From a somewhat empiric standpoint a value of $\mu = 20 \,.\, 10^{-19}$ E.S.U. is obtained from the refractive index (Gans, *Ann. de Phys.* LXIV. 481, 1921; Smyth, *Phil. Mag.* XLV. 849, 1923; *J.A.C.S.* XLVI. 2153, 1924). Whilst existing data on the temperature coefficient of the dielectric constants of organic acids either in the state of attenuated non-associated vapours or in solution in non-polar solvents are insufficient to evaluate μ, for the aromatic acids the contribution of the —COOH group to the molecular electric moment appears to be $9{\cdot}0 \,.\, 10^{-19}$ E.S.U. (Debye, *Dipolmoment und chemische Struktur*, Herzel, 1929, p. 30).

Still a third approximate method of computation is available from a consideration of the equation of state of the film. This was shown in Ch. III to be

$$F(A - B) = iRT,$$

where $\frac{1}{i}$ represents the lateral molecular cohesion. If this adhesion be purely electrical in origin and equal to ψ we may write as the equation of state

$$F(A - B) = RT - \psi,$$

whence $$1 - i = \frac{\psi}{RT}.$$

If the mean potential energy of a molecule in the film be approximately $\frac{9\mu^2}{2r^3} = \frac{9}{2}\mu^2 A^{\frac{3}{2}}$ (see p. 306 and Tamamushi, *Bull. Soc. Chem. Japan*, XI. 300, 1927), then we obtain

$$1 - i = \frac{9\mu^2 A^{\frac{3}{2}}}{2kT}.$$

Rideal and Schofield obtained values of i ranging from 0·73 for butyric acid to 0·21 for myristic acid. It is clear that this simple assumption of the constancy of the ratio of potential to kinetic energy in all states of the film cannot be regarded as correct, but assuming its applicability to the commencement of the expanded or liquid state of the film, i.e. at *ca.* $r = 5$ Å., we obtain for a value of $kT = 4 \,.\, 10^{-14}$ ergs the following values.

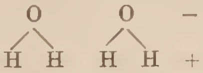
Acid	$1 - i$	r in Å.	μ E.S.U. $\times 10^{19}$
n-Butyric	0·27	5·0	5·4
Valeric	0·37	,,	6·3
Caproic	0·57	,,	7·9
Caprylic	0·54	,,	7·7
Capric	0·65	,,	8·4
Lauric	0·77	,,	9·1
Myristic	0·79	,,	9·3

These values are in fair agreement with those obtained by the methods indicated above.

The experimental data do not permit of a decision as to how far the difference between the maximum value of μ, viz. $3{\cdot}7 \,.\, 10^{-19}$ E.S.U., obtained by the method of surface potentials and that obtained from the dielectric constant, viz. 9·0 . 10^{-19} E.S.U., can be ascribed to the fact that in the method of surface potentials only the resolved component of the electric moment is measured and this whilst attaining a maximum value at certain compressions may be restrained by molecular orientation due to adhesional forces from attaining the maximum possible value. The other factor to be considered is the possible mutual polarisation of the carboxylic group with the water molecules in the substrate. That the effects of the moment of the carboxylic group are detectable at some distance in the interior of the liquid was shown by Schulman who measured the contribution of the ionic double layer brought into existence by the attraction of the dipoles for the ions in the solution. The magnitude of this double layer was found to be dependent on the state of the film and not on the extent of the molecular packing in the film and would in certain cases, e.g. on capillary active citrate buffers, approach quite large values equivalent to nearly half the moment contributed by the molecule in the film.

The sign as well as the magnitude of the change in the air-liquid P.D. on the addition of a capillary active solute provides interesting information on the surface arrangement of the active or polar group.

Water is probably feebly polar and may be imagined to orientate itself in the form



Introduction of a chlorine atom into the organic radical reduces according to Frumkin the positive charge and may actually produce a negative value; thus we obtain

Compound	ΔV_∞ in m.v.
Acetic acid	+ 285
Monochloracetic acid ...	− 150
Dichloracetic acid ...	− 280
Trichloracetic acid ...	− 600
Alcohol	+ 380
Ethylene monochlor hydrin	− 30
Ethyl acetate	+ 610
Ethyl monochlor acetate ...	+ 410

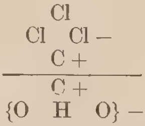
Evidently the alteration of the ΔV_∞ values with introduction of chlorines cannot be attributed to its effect on the alteration of the strengths of the substituted acetic acids, for alcohols and esters exhibit similar changes. In order to examine the moment of the C—Cl union, some idea of the nature of its orientation at a water-air interface must be obtained.

Frumkin has obtained the following data for the effect of normal solutions of the following salts on the surface tension of water:

Salt	$\Delta\sigma$
Na acetate	+ 0·4
Na monochlor acetate	+ 0·1
Na dichlor acetate ...	− 1·9
Na trichlor acetate ...	− 7·2

Surface adsorption thus increases with the introduction of chlorine atoms or energy is required to pull a chlorine atom from the surface to the interior.

We may conclude that trichlor acetic acid is orientated as follows:



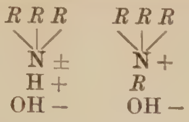
$$\begin{array}{c} \text{Cl} \\ \text{Cl}\quad\text{Cl}- \\ \text{C}+ \\ \hline \text{C}+ \\ \{\text{O}\quad\text{H}\quad\text{O}\}- \end{array}$$

That the chlorine is negative respective to the carbon may be shown in the case of chloroform, but both methyl iodide and ethyl iodide were found to be too insoluble and volatile to give any definite values.

The iodo and brom acetic acids gave similar results to the chlor derivatives.

The value of ΔV_∞ for triethylamine ($\Delta V_\infty = +$ 630 m.v.) appears to be identical with that for ammonia and the various substituted ammonias; substitution thus appears to exert no effect on the moment of this molecule.

Thus we may depict its orientation as follows:



where R may be an alkyl group or a hydrogen.

The potential is raised for compounds of the type NR_4OH which may be represented as indicated above.

The preferential adsorption of ions at a benzene-water interface has been shown by Deutsch (*Zeit. physikal. Chem.* CXXXVI. 353, 1928) (see also Thiel, *Zeit. Elektrochem.* XXXV. 266, 1929) by shaking up indicators with benzene and buffered aqueous solutions; variations of the order of $P_H = 1$ were observed by the difference of indicator colour at the interface.

Electrolytes.

With the exception of the alkaline hydroxides NaOH, KOH and possibly the fluorides KF, NaF, the direction of the E.M.F. indicates that all monovalent anions are repelled from the free surface of waters less than the cations $\text{Li}^{\cdot}$, $\text{Na}^{\cdot}$, $\text{K}^{\cdot}$, $\text{Cs}^{\cdot}$. Divalent ions show on the other hand only slight differences. As has already been noted the fact that the surface tension of water is raised by the addition of salts indicates that repulsion of the salt as a whole from the surface must take place.

According to Frumkin (*Koll. Zeit.* XL. 9, 1926) the behaviour of the cations $\text{Li}^{\cdot}$, $\text{Na}^{\cdot}$, $\text{K}^{\cdot}$, $\text{Cs}^{\cdot}$ is almost identical; the specific differences appear to lie in the nature of the anions. At the same concentrations these cause E.M.F.'s in the order

$$\text{CNS}' > \text{ClO}_4' > \text{I}' > \text{MnO}_4' > \text{NO}_3' > \text{CNO}' > \text{Br}',$$
$$\text{BrO}_3' > \text{CN}' > \text{Cl}' > \text{OH}',\ \text{F}';$$

thus the extent to which the anions are repelled from the surface decreases as we pass from right to left in this series. In agreement with this it is found that the extent to which potassium salts at normal concentrations raise the surface tension of water falls as we pass from KF to KBr in the manner shown on p. 344. In the case of KCNS the surface tension is actually lowered so that the CNS' is apparently actually attracted to the free surface, in agreement with the observation on the large electromotive force.

Salt	$\Delta\sigma$ for normal concentration
KF	1·83
KCl	1·46
KNO_3	1·12
KBr	1·06

The general distribution of ions on the free surface may be represented as

$$\begin{array}{cc} \overset{-}{\mathrm{Cl}} & \overset{-}{\mathrm{Cl}} \\ \overset{+}{\mathrm{K}} & \overset{+}{\mathrm{K}} \end{array}$$

the free surface possessing a net negative charge.

The monobasic acids all show a more marked E.M.F. than the corresponding salts. They also lower the surface tension of water. The anions appear therefore to approach nearer to the surface in the presence of $H^{\cdot}$ ions than $K^{\cdot}$ ions. In KOH the E.M.F. is reversed, the $K^{\cdot}$ being less repelled from the surface than the OH'. Ammonium salts behave like potassium salts except that ammonia is quite different from the other bases, giving a strong reversed E.M.F. and lowering the surface tension of water like an organic compound.

It may be noted that similar lyotropic series for the anions have been observed at other interfaces in addition to the air-water interface. Beutner's series (see p. 364) for the oil-water interface adsorption is

$$CNS' > I' > NO_3', \ Br' > Cl' > SO_4'',$$

and Gouy (see p. 314) obtained for the adsorption at a neutral mercury surface the order

$$HS' > I' > CNS' > CN' > Br' > NO_3' > Cl' > OH'.$$

Ions such as S'', HS', I' and CN' are probably somewhat displaced owing to the "chemical" attraction they exert for mercury.

12. Electrification at liquid-liquid interfaces.

Diffusion potentials.

In a cell of the type

$$\begin{array}{c|c|c|c} M & \underset{c_1}{MX} & \underset{c_2}{MX} & M \\ \multicolumn{4}{c}{\qquad V_1 \qquad V_2 \qquad V_3} \end{array}$$

we note that the total electromotive force of the cell is the algebraic sum of three potential differences or

$$V = V_1 + V_2 + V_3.$$

The two electrode potentials V_1 and V_3 are according to the Nernst conception of electrolytic solution pressure given by the expression

$$V_1 = \frac{RT}{nF} \log \frac{P}{f_1 c_1},$$

where $f_1 c_1$ is the activity of the n-valent M ion in the first electrolyte, and

$$V_3 = \frac{-RT}{nF} \log \frac{P}{f_2 c_2},$$

thus

$$V_1 + V_3 = \frac{RT}{nF} \log \frac{f_2 c_2}{f_1 c_1}.$$

Since the observed electromotive force of the cell is V,

$$V_2 = V - \frac{RT}{nF} \log \frac{f_2 c_2}{f_1 c_1}.$$

The diffusion potential V_2 can be calculated in the following manner due to Nernst (*Zeit. physikal. Chem.* II. 611, 1888; IV. 129, 1889):

$$\begin{array}{c|c} M^{\cdot} & M^{\cdot} \\ X' & X' \\ c_1 & c_2 \end{array}$$

If we imagine that F coulombs of electricity be transported across a boundary separating two solutions of a monovalent electrolyte MX of concentrations c_1 and c_2, the electrical work performed will be $V_2 F$, where V_2 is the difference of potential between the two solutions.

A fraction $\frac{u}{u+v}$, where u is the mobility of the cation and v the mobility of the anion, of the total current is carried by the cation and a fraction $\frac{v}{u+v}$ by the anion. The fraction $\frac{u}{u+v}$ of cation is transported from a solution of concentration c_1 to that of c_2, whilst the fraction $\frac{v}{u+v}$ is transported in the opposite direction. The net osmotic work that must be performed by the transportation of cation and anion in this manner is thus

$$RT \frac{u}{u+v} \log \frac{f_2 c_2}{f_1 c_1} - RT \frac{v}{u+v} \log \frac{f_2 c_2}{f_1 c_1},$$

or
$$RT\frac{u-v}{u+v}\log\frac{f_2c_2}{f_1c_1}.$$

The electrical work and osmotic work both performed in a perfectly reversible manner are equal, thus

$$V_2F = RT\frac{u-v}{u+v}\log\frac{f_2c_2}{f_1c_1},$$

$$\therefore\ V_2 = \frac{RT}{F}\frac{u-v}{u+v}\log\frac{f_2c_2}{f_1c_1}.$$

For large values of the difference between the mobility of the cation and that of the anion, the diffusion potential V_2 will by no means be negligible. Both hydrogen and hydroxyl ions possess exceptionally large mobilities in aqueous solution and thus diffusion potentials between solutions of different concentrations of both acids and alkalis may assume large values as indicated by the following data for the values of V_2 between solutions of electrolytes of concentration ratios 10 : 1.

Electrolyte	u	v	V_2 in millivolts
HCl ...	318·0	65·4	+ 37·8
NaOH	43·55	174·0	− 34·6
KCl ...	64·67	65·44	− 0·4
NH_4NO_3	64·0	61·78	+ 1·1

It will be noted that liquid junction diffusion potentials can be eliminated almost completely by ensuring that the bulk of the current is carried by cations and anions possessing equal mobilities, e.g. KCl or NH_4NO_3. Thus by inserting a saturated solution of either of these salts between any other pair of solutions forming a junction, the liquid junction potential can be greatly reduced.

The more general problem of the magnitude of the liquid junction existing between the following types of ionic solutions

$$\begin{array}{c|c} M^{\cdot}c_1 & M^{\cdot}c_2 \\ X'c_1 & Y'c_2 \end{array} \qquad \begin{array}{c|c} M^{\cdot} & N^{\cdot} \\ X' & X' \end{array} \quad \text{and} \quad \begin{array}{c|c} M^{\cdot} & N^{\cdot} \\ X' & Y' \end{array}$$

has been investigated by Planck (*Wied. Ann.* XL. 561, 1890), Johnson (*Ann. der Physik*, XIV. 995, 1904), G. N. Lewis (*J.A.C.S.*

XXXI. 363, 1907), Henderson (*Zeit. physikal. Chem.* LIX. 118, 1907; LXIII. 325, 1908) and Bjerrum (*Zeit. f. Elektrochem.* XVII. 391, 1911).

If the two electrolytes of concentration c_1 and c_2 are monovalent and the ionic mobilities u_1, v_1 and u_2, v_2 respectively, then

$$V_2 = \frac{RT}{F} \log \xi,$$

where ξ is defined by the relationship

$$\frac{\xi c_2 u_2 - c_1 u_1}{c_2 v_2 - \xi v_1 c_1} = \frac{\log \frac{c_2}{c_1} - \log \xi}{\log \frac{c_2}{c_1} + \log \xi} \cdot \frac{\xi c_2 - c}{c_2 - \xi c_1}.$$

In those cases where $c_1 = c_2$ we find $\xi = \frac{u_1 + v_1}{u_2 + v_2}$, and since the conductivities of solutions are proportional to the ionic mobilities at dilutions of equal dissociation, we find for strong and equally dissociated electrolytes the following:

$$V_2 = \frac{RT}{F} \log \frac{u_1 + v_1}{u_2 + v_2} = \frac{RT}{F} \log \frac{\lambda_{\infty_1}}{\lambda_{\infty_2}} = \frac{RT}{F} \log \frac{\lambda_1}{\lambda_2}.$$

As an indication of the magnitudes of such diffusion potentials the following values may be given:

Electrolyte junction		V_2 in millivolts
HCl	KCl	+ 26·8
NaOH	NaCl	− 17·3
NaCl	KCl	− 4·4
NH_4NO_3	KCl	0·6

It is clear that in junctions which are sharp and well defined, the transport from one liquid to another will take place by means of only one kind of cation and one anion, but where the junctions are diffuse and a relatively gradual conversion from one pure electrolyte to the other occurs, the transport ratio will be fluctuating from one extreme value to the other and the above equation of Planck developed on the assumption of a sharp and well-defined boundary will not be rigid. Henderson and Cumming (*loc. cit.*) have investigated this second type of boundary. For two monovalent electrolytes of concentrations c_1 and c_2 and ionic mobilities u_1, v_1 and u_2, v_2, Henderson's equation reduces to the following:

$$V_2 = \frac{RT}{F}\frac{(u_1c_1 - v_1c_1) - (u_2c_2 - v_2c_2)}{(u_1c_1 + v_1c_1) - (u_2c_2 + v_2c_2)} \log \frac{u_1c_1 + v_1c_1}{u_2c_2 + v_2c_2},$$

which undergoes still further simplification when $c_1 = c_2$,

$$V_2 = \frac{RT}{F}\frac{(u_1 - v_1) - (u_2 - v_2)}{(u_1 + v_1) - (u_2 + v_2)} \log \frac{u_1 + v_1}{u_2 + v_2}$$

or

$$V_2 = \frac{RT}{F}\frac{(u_1 - u_2) - (v_1 - v_2)}{(u_1 - u_2) + (v_1 - v_2)} \log \frac{u_1 + v_1}{u_2 + v_2}.$$

This equation is evidently identical with that of Planck only when $u_1 = u_2$ or $v_1 = v_2$, i.e. the two electrolytes contain a common or an equimobile ion.

Diffusion or liquid junctions are thus not clearly defined since the potential difference is dependent on the sharpness of the junction. Uniformly sharp junctions have been obtained by Lamb and Larson (*J.A.C.S.* XLII. 229, 1920) by allowing one liquid to flow against the other, whilst Bjerrum (*Zeit. f. Elektrochem.* LIII. 428, 1905) has obtained a relatively diffuse junction by the insertion of a sand diaphragm between the two electrolytes.

Membrane potentials.

When an interfacial film increases in thickness until it acquires the characteristics of a bulk phase it may under certain circumstances behave as a membrane, possessing more or less selective permeability for the different constituents of the two homogeneous phases on each side. We may distinguish at least two types of membranes, one in which the selective permeability is attributable to a sieve-like structure permitting the passage of certain constituents only, through holes or interfibrillar canals, the other in which the membrane bulk phase is homogeneous and its selective permeability is attributable to different solubilities in the membrane material of the different constituents of the bulk phases.

When the homogeneous phases on each side contain electrolytes insertion of membranes of either type between the phases may modify profoundly the normal diffusion potential.

Molecular sieve membranes.

The modification of the normal diffusion potential produced by the introduction of a membrane of the molecular sieve type is due to an alteration of the velocities of the single ions diffusing across or through the membrane. If the ion be sufficiently large, e.g. a protein ion or an anion of congo red, the membrane will be impermeable to it; this limiting case, investigated by Donnan, will be dealt with in detail later.

The relative modification of the ionic velocities can be calculated with the aid of the equation

$$V = \frac{u - v}{u + v}\frac{RT}{nF}\log\frac{f_2 c_2}{f_1 c_1}$$

from the observed potential difference and that of the true diffusion potential. Thus Prideaux (Prideaux and Crookes, *Trans. Farad. Soc.* xx. 37, 1924) found that the liquid junction potentials between solutions of sodium benzoate and salicylate at different concentrations were enhanced by the interposition of a parchment membrane, due to a relative decrease of the anionic velocity in the membrane to 0·74 for the benzoate and 0·66 for the salicylate ions of their respective values in aqueous solution.

The cause of the anionic retardation is not purely mechanical since the ion retarded is that which is preferentially adsorbed by the material of the membrane, a rule true irrespective of the size of the ion. Prideaux (*Trans. Farad. Soc.* Dec. 1928) observed that with parchment membranes which acquire a negative charge in solution the slow moving anions in sodium benzoate and phenyl acetate were retarded and the concentration potential raised, but with piperidine hydrochloride in which the cation is least mobile the anion is again retarded and the concentration potential this time is lowered.

The normal process of diffusion of anion and cation together can be pictured as being modified in the membrane by the formation of a Helmholtz or Stern type of double layer on the walls of the capillaries through which diffusion is taking place. The layer of solution adjacent to the walls contains a preponderance of ions of one kind moving with a reduced velocity.

The most exhaustive study of the effects on diffusion and diffusion potentials which a membrane can produce has been made by Michaelis and his co-workers (*J. Gen. Physiol.* 1926 and onwards; *Coll. Symp. Monograph*, v. 1927; *Bull. Nat. Research Council*, No. 69) with membranes of collodion films.

Such fine sieve membranes as used by Michaelis are only slightly permeable and the relative diffusion coefficients of organic compounds through them follow the same order as in free diffusion, but decrease much more rapidly with increasing molecular weight as exemplified in the following table:

	Relative coefficient of diffusion in membrane	Relative molecular weight
Methyl alcohol	9·2	0·53
Ethyl alcohol ...	3·0	0·77
Propyl alcohol	1·0	1·00
Butyl alcohol ...	0·8	1·23
Glycerin ...	0·22	1·53
Chloral hydrate	0·11	2·75
Monochlorhydrin	0·067	1·84
Glucose ...	0·00	3·3

Collodion is unaffected by dilute acids and salts and, except in the presence of positively charged dyes, multivalent cations and high hydrogen ion concentrations, it carries a high negative charge. The anions are consequently strongly adsorbed and as a result the diffusion of salts such as potassium chloride across the membrane into pure water is too slow to be measured, since the potassium ions are bound electrostatically to the strongly adsorbed chlorine ions. If however the water be replaced by sodium nitrate exchange of cations across the membrane can occur and a measurable diffusion takes place; the proportion of $\dot{K}$ to Cl′ diffusing is as 10 : 1, whereas with a normally permeable large pore collodion membrane the ions diffuse in equal proportions.

Michaelis employed as a standard measure of the membrane permeability the characteristic concentration potential (the C.O.P.) of the cell

$$\frac{N}{100}\,\text{KCl} \,\Big|\, \text{Membrane} \,\Big|\, \frac{N}{10}\,\text{KCl}.$$

The maximum value of the potential corresponding to zero anionic mobility is given by

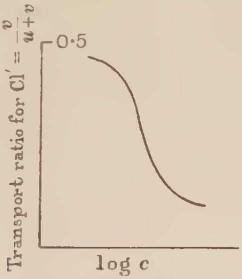
$$E = \frac{RT}{nF} \log \frac{c_2}{c_1} = 55 \text{ millivolts at } 15^\circ \text{ C.}$$

In confirmation of this value obtained with KCl Michaelis found that salts containing other univalent cations including the hydrogen ion gave values for the C.O.P. of from 45–55 m.v. irrespective of the nature of anions.

It is interesting to note that the membrane potential for a given concentration ratio varies over the range of concentration employed, approaching its theoretical value as dilution proceeds. If the transport number of the anions are calculated from the E.M.F. measurements using the equation

$$\frac{v}{u+v} = 0{\cdot}5 - \frac{V \text{ (millivolts)}}{2 \times 58 \times \log_{10} \frac{c_2}{c_1}} \text{ at } 20^\circ \text{ C.}$$

we obtain for KCl the following curve.



It is clear that the transport number for an ion within the membrane varies much more with the concentration than it does in free aqueous solution and that the decreasing mobility of the anion with decreasing concentration is paralleled by the increased relative adsorption of the ions by the collodion as the dilution proceeds. Michaelis has obtained a fair confirmation of these values for the transport numbers by application of Hittorf's direct method of measurement.

In support of this mechanism of membrane potential Michaelis has measured the E.M.F.'s of two series of $\frac{N}{10}$ solutions in one of which each pair has a cation in common and in the other an anion. In the former case the potentials were negligible, in the latter considerable and differed greatly from the ordinary diffusion potentials. The potential differences are thus due only to the difference between the mobilities of the opposed cations and the relative mobilities of the cations in the membrane and in free aqueous solution.

Mond and Hoffmann (*Pflüg. Archiv*, CCXX. 194, 1928) have extended Michaelis' technique to the study of collodion membrane dyed with Rhodamin B which ensures the preferential adsorption of cations on the walls. The contrast between the relative cationic mobilities in the undyed negatively charged membrane and the relative anionic mobilities in the positively charged dyed membrane and the ionic mobilities in solution are shown in the following table:

Negative membrane Michaelis				Positive membrane Mond and Hoffmann		
Cation	*u* in membrane	*u* in water	Water of hydration	Anion	*v* in membrane	*v* in water
Li	0·048	0·52	15	SCN	10·8	0·86
Na	0·14	0·65	9	NO_3	7·57	0·94
K	1·0	1·0	5	I	3·54	1·01
Rb	2·8	1·04	3	Br	2·21	1·025
H	42·5	4·9	1	Cl	1·0	1·0
				Ac	0·728	0·538
				SO_4	0·221	—

It will be noted that the order of the anionic mobilities in the membrane does not follow that observed in water, possibly due to differential adsorption of the anions on the membrane surface where the cations are bound. A further difference is noted in the behaviour of these two types of membranes in that as we have noted on dilution the E.M.F. of the concentration chain KCl 1 : 10 increases in the case of the negative membrane towards the theoretical value, whilst with the positive membrane the reverse is the case. A membrane half stained with Rhodamin B is, according to Höber and Hoffmann (*Pflüg.*

Archiv. CCXX. 888, 1928), selectively permeable both to anions and cations.

Membranes composed of amphoteric materials such as gelatine (see Fujita, *B.Z.* CLXII. 245, 1925) and various proteins (see p. 408) will impose a retardation both on anions and cations dependent on the hydrogen ion concentration in the membrane. On the acid side of the isoelectric point the ordinary diffusion potential is reversed in sign; near the isoelectric point it is least modified and on the basic side the E.M.F. is increased, the dilute solution becoming more positive. These observations qualitatively agree with the theory developed above.

Donnan membrane potentials.

We have noted that the limiting case for a molecular sieve membrane is obtained when one ion possesses zero mobility within the membrane, i.e. the membrane is impermeable to one ion. The theory of the membrane potential developed under these conditions was first given by Donnan (*Zeit. Elektrochem.* XVII. 572, 1911).

A vessel is divided into two halves by means of a membrane; on one side of the membrane a solution of a salt, of which both ions, e.g. $\mathrm{Na}^{\bullet}$ and Cl', can pass through the membrane, is placed. To the other side a salt for one ion of which the membrane is permeable, and to the other impermeable, e.g. the sodium salt of congo red $\mathrm{Na}^{\bullet}\ R'$, is added.

If it be assumed that complete electrolytic dissociation of each salt occurs, and that there are equal quantities of liquid on each side of the membrane, sodium chloride will commence to diffuse from one side to the other.

We can represent diagrammatically the initial and final states of the system as follows:

$$\begin{array}{r|l} c_2\,\mathrm{Na}^{\bullet} & \mathrm{Na}^{\bullet}\ c_1 \\ c_2\ \mathrm{Cl}' & R'\ \ c_1 \\ \multicolumn{2}{c}{\text{Initial}} \end{array} \qquad \begin{array}{r|l} c_2-x\,\mathrm{Na}^{\bullet} & \mathrm{Na}^{\bullet}\ c_1+x \\ c_2-x\ \ \mathrm{Cl}' & \mathrm{Cl}'\,x \\ & R'\,c_1 \\ \multicolumn{2}{c}{\text{Final}} \end{array}$$

At equilibrium, the change in free energy produced by the reversible transport of a small quantity of sodium chloride δn

from one side to the other at constant temperature and volume is zero, or

$$\delta n\, RT\left\{\log\frac{c_1+x}{c_2-x}+\log\frac{x}{c_2-x}\right\}=0,$$

or

$$(c_1+x)(x)=(c_2-x)^2,$$

or

$$x=\frac{c_2{}^2}{c_1+2c_2} \text{ or } \frac{x}{c_2}=\frac{c_2}{c_1+2c_2} \text{ and } \frac{c_2-x}{x}=\frac{c_1+c_2}{c_2}.$$

If c_2 is small compared to c_1, we obtain

$$\frac{c_2-x}{x}=\frac{c_1}{c_2}.$$

The sodium chloride will thus distribute itself on either side of the membrane in a ratio which is a function of the concentrations of both salts.

The following table gives an idea of the magnitude of influence of the colloid on the distribution ratio of the sodium chloride:

Initial concentration of Congo red c_1	Initial concentration of sodium chloride c_2	$\frac{c_2}{c_1}$	$100\frac{x}{c_2}$	$\frac{c_2-x}{x}$
0·01	1	100	49·7	1·01
0·1	1	10	47·6	1·1
1	1	1	33	2
1	0·1	0·1	8·3	11
1	0·01	0·01	1	99

This system has been investigated in some detail by Azuma and Kameyama (*Phil. Mag.* L. 1269, 1925).

If the concentration of the diffusible electrolyte is small, relative to that of the colloid electrolyte, only a small quantity of salt will diffuse across the membrane; whilst if the electrolyte is present in relatively large quantities, there will obtain practically an equal distribution on either side of the membrane. A similar treatment permits of the calculation of the equilibrium distribution of a salt containing no ion in common with that of the colloid electrolyte.

If pure water be placed in one compartment and the colloid electrolyte in the other, the diffusible ion will penetrate with an accompanying hydroxyl ion resulting in the formation of acid in one compartment, and alkali in the other,

$$\underset{\text{Initial}}{\begin{array}{cc|c} \mathrm{Na}^{\bullet} & R' & \mathrm{H_2O} \\ c_1 & c_1 & \end{array}} \qquad \underset{\text{Final}}{\begin{array}{cc|cc} c_1 - x & \mathrm{Na}^{\bullet} & \mathrm{Na}^{\bullet} & x \\ y & \mathrm{H}^{\bullet} & \mathrm{OH}' & x \\ c_1 & R' & & \end{array}}$$

As before, we obtain the expression for the mass law by application of the principle of virtual work to the system in equilibrium. If (x) be the concentration of hydroxyl ions corresponding to a concentration y of hydrogen, viz.:

$$(c_1 - x)\,(y) = x^2.$$

If the ionisation constant of water be K_w, then $K_w = (x)\,(y)$, or

$$x^2 = \frac{(c_1 - x)\,K_w}{x},$$

or

$$x^3 = (c_1 - x)\,K_w.$$

For small hydrolysis, where c_1 is great compared with x,

$$x^3 = c_1 K_w \quad \text{or} \quad x = \sqrt[3]{c_1 K_w}.$$

The value of K_w at ordinary temperatures is *ca.* 10^{-14}; the percentage hydrolysis $100\,\frac{x}{c_1}$ of the colloidal electrolyte can thus be computed from the bulk concentration and is evidently very small, e.g. for $c = 0{\cdot}01$, $100\,\frac{x}{c_1} = 0{\cdot}05\,\%$. The insertion of the membrane thus gives rise to an unequal distribution of the electrolyte on either side, to an alteration in the apparent osmotic pressure of the colloidal electrolyte (Donnan and Harris, *J.C.S.* XCIX. 1559, 1911; Donnan and Allmand, *ibid.* CV. 1941, 1914; Donnan and Garner, *ibid.* CXV. 1313, 1919) and also to a potential difference.

The magnitude of the potential difference can be calculated by consideration of the work done in the isothermal transfer of a small quantity of electricity $(F\delta n)$ from one solution to the other when equilibrium is obtained.

If $n\,\delta n$ mols of Na˙ are transferred from one side to the other and $(1 - n)\,\delta n$ mols of Cl′ in the reverse direction, $\frac{n}{1-n}$ being the transport values of the ions, the osmotic work done is

$$n\,\delta n\,RT\log\frac{c_2 - x}{c_1 + x} + (1 - n)\,\delta n\,RT\log\frac{x}{c_2 - x}.$$

The electrical work done, if V_1 and V_2 be the potentials of the solution, is $(V_2 - V_1)\,F\,\delta n$, which must be equal to the above.

We have seen that at equilibrium (p. 354)

$$\frac{c_2 - x}{c_1 + x} = \frac{x}{c_2 - x} = \lambda \text{ say;}$$

hence the potential across the membrane

$$V_2 - V_1 = \frac{RT}{F}\log\frac{1}{\lambda}.$$

We have seen that $\frac{c_2 - x}{x} = \frac{c_1 + c_2}{c_2}$; hence $\lambda = \frac{c_2}{c_1 + c_2}$.

The potential difference across the membrane is accordingly

$$V_2 - V_1 = \frac{RT}{F}\log\left(1 + \frac{c_1}{c_2}\right) = \cdot058\log\frac{c_1}{c_2}$$

for a small $c_2 : c_1$ ratio.

The magnitude of this membrane potential is discerned from the following figures:

$\frac{c_1}{c_2}$	$V_2 - V_1$
10	·058
100	·116
1000	·174
10000	·232

and potentials of this order of magnitude have been observed by Donnan and Green (*Proc. Roy. Soc.* A, XC. 450, 1914) and Kameyama (*Phil. Mag.* L. 849, 1925) at a copper ferrocyanide membrane.

It is evident that increasing the quantity of diffusible electrolyte in the solution decreases the membrane potential, a phenomenon observed in the case of Procter and Wilson (*J.C.S.* CIX. 1317, 1916) for tannin and by Loeb (*J. Gen. Physiol.* III. 607;

III. 691; III. 827; IV. 33; IV. 97, 1921) (see Ch. IX) in the case of gelatine.

Numerous applications of Donnan's theory have been made to investigations on the proteins; thus Sporing (*J.C.S.* CXXV. 2316, 1924) has determined the dissociation of basic sodium caseinate from the system

$$\begin{array}{r|l} \text{Basic sodium caseinate} & \\ \text{Sodium chloride} & \text{Sodium chloride} \end{array}$$

Loeb and his co-workers have likewise examined systems containing proteins such as gelatine, egg-albumin, edestin, globulin and acids and salts.

Thus in the case of the system

$$\begin{array}{l|l} z\ \overset{+}{\text{Gelatine}} & \overset{+}{\text{H}}\ x \\ y\ \overset{+}{\text{H}} & \text{Cl}'\ x \\ (y+z)\ \text{Cl}' & \end{array}$$

We have seen that the membrane potential is given by

$$V = \frac{RT}{nF} \log\left(1 + \frac{z}{y}\right).$$

The ratio $\frac{z}{y}$ may be varied by changing either the P_{H} of the system or the protein concentration. For 100 c.c. of 1 % isoelectric gelatine the following data were obtained.

c.c. 0·1*N* HCl	1·0	2·0	4·0	6·0	8·0	10·0
Hydrogen electrode P.D.	24·7	31·0	34·5	34·5	27·0	25·8
Membrane P.D.... ...	24·0	32·0	33·0	32·5	26·0	24·5
c.c. 0·1*N* HCl	12·5	15·0	20·0	30·0	40·0	50·0
Hydrogen electrode P.D.	18·8	14·0	7·6	5·9	4·1	2·3
Membrane P.D.... ...	16·5	11·2	6·4	4·8	3·7	2·1

The most exhaustive thermodynamical examination of the conditions of the Donnan equilibrium has been made by Hückel (*Koll. Zeit.* XXXVI. 204, 1928)

$$\begin{array}{r|l} \text{Na}\ c_2 & R\ c_1 \\ \text{Cl}\ c_2 & \text{Cl}\ c_3 \\ & \text{Na}\ c_1 - c_3 \end{array}$$

He shows that for dilute solutions in the above system the accurate form of the Donnan equilibrium is given by

$$2\left[(c_1 + c_3) - 2c_2\right]\frac{v_1 + v_2}{v_0} = 2\log c_2 - \log c_1(c_1 + c_3).$$

Since in general $v_1 + v_2$ is not very different from the original total volume of solvent v_0 and c_1, c_2, c_3 are small compared with unity, the above equation reduces to $2\log c_2 - \log c_1(c_1 + c_3) = 0$, which is the form given by Donnan, and the potential difference

$$V = \frac{v_2}{v_0} KT\left[2(c_1 + c_3) - 2c_1\right] - KT\log\frac{c_2}{c_1},$$

or approximately

$$V = KT\log\frac{c_1}{c_2} = KT\log\frac{c_2}{c_1 + c_3}.$$

Donnan's theory may be applied not only to the case of non-diffusible ions but also to the case of colloidal solutions where the colloidal particle has acquired a charge by the selective adsorption of ions from the solution. The adsorption of ions by colloidal solutions of chromium hydroxide (Bjerrum, *Zeit. physikal. Chem.* CX. 656, 1924), sulphur and silicic acid (Rinde, *Phil. Mag.* (75), I. 32, 1926) have been examined and shown to fulfil these conditions (Ganguly and Krishnamurti, *Trans. Farad. Soc.* XXIV. 401, 1928).

We may cite the following data obtained by Bjerrum for the distribution of hydrogen chloride on each side of a membrane, one compartment containing colloidal chromium hydroxide.

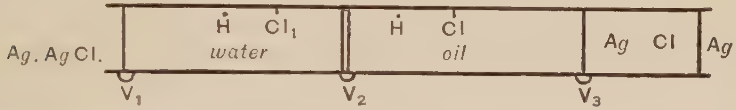
Original HCl concentration	Cr	Membrane potential m.v.	Chlorine ion potential difference for solutions m.v.	Chlorine ions bound per $Cr^{\cdots}$ atom	Chlorine and hydrogen ions bound per $Cr^{\cdots}$ atom
0·01 N	0·076	6·4	6·0	0·22	0·253
0·005 N	0·049	7·4	8·8	0·21	0·24

Homogeneous membranes.

Modified membrane potentials are noted in the case of the interface between two immiscible liquids, e.g. oil and water, owing to the unequal distribution of the ions of a dissolved electrolyte between the two media (see Nernst and Riesenfeld, *Ann. der Physik* (4), VIII. 600, 1902; Haber, *ibid.* (4), XXVI. 927, 1908; Haber and Klemenziewicz, *Zeit. physikal. Chem.* LXVII. 385, 1909; Michaelis, *Dynamik der Oberflächen*, 1909; Beutner, *Die Entstehung elektrischer Ströme in lebenden Geweben*, 1920).

The existence of the liquid potential at a liquid-liquid interface can be demonstrated in the following way.

An electrolyte, e.g. HCl, is shaken up with the two immiscible solvents, water and oil, until the partition equilibrium is arrived at.



If a hydrogen electrode be immersed in each solution since the system is in equilibrium, the potential difference between these electrodes must be zero. Similarly for the chlorine ion, there will be a zero potential difference between two silver-silver chloride electrodes immersed in the two media.

The P.D. of a hydrogen electrode immersed in a solution of hydrogen ion activity $fc_{\dot{H}}$ is given by the expression

$$V = \frac{RT}{nF} \log \frac{fc_{\dot{H}}}{fc_{0\dot{H}}},$$

where $fc_{0\dot{H}}$ is the hydrogen ion activity of a solution for which zero potential difference exists, corresponding to the electrolytic solution pressure of the ion in that particular medium.

In the absence of an interfacial potential difference between the two media we obtain as the E.M.F. of the cell

$$V = \frac{RT}{nF} \log \frac{fc_{\dot{H}a}}{fc_{0\dot{H}a}} - \frac{RT}{nF} \log \frac{fc_{\dot{H}b}}{fc_{0\dot{H}b}},$$

where the suffixes a and b refer to the two media.

Since $V = 0$ at equilibrium $\frac{fc_{\dot{H}a}}{fc_{\dot{H}b}} = \frac{fc_{0\dot{H}a}}{fc_{0\dot{H}b}}$.

Similarly for the chlorine ions $\frac{fc_{\mathrm{Cl}a}}{fc_{\mathrm{Cl}b}} = \frac{fc_{0\mathrm{Cl}a}}{fc_{0\mathrm{Cl}b}}$.

The partition coefficient of either ion should thus be independent of that of the other. This is evidently not the case, since the partition coefficient of electrolytes containing a common ion, e.g. the chlorine ion, varies with the nature of the cation; thus the oil-water ratio for aniline hydrochloride is much greater than that for sodium chloride.

In general, the interfacial potential difference will be finite and equal to

$$\begin{aligned} V_{\mathrm{H}} &= \frac{RT}{nF}\left(\log\frac{fc_{\dot{\mathrm{H}}a}}{fc_{\dot{\mathrm{H}}b}} + \log\frac{fc_{0\,\dot{\mathrm{H}}b}}{fc_{0\,\dot{\mathrm{H}}a}}\right) \\ &= \frac{RT}{nF}\log\frac{fc_{\dot{\mathrm{H}}a}}{fc_{\dot{\mathrm{H}}b}} + L, \end{aligned}$$

where L is a constant.

The partition coefficient of one ion, e.g. the hydrogen considered as distributing itself between the two media independently of the other, is given by the expression $\frac{fc_{0\,\dot{\mathrm{H}}a}}{fc_{0\,\dot{\mathrm{H}}b}}$, which is the limiting distribution which the hydrogen ion attempts to establish, but is prevented from doing so owing to the presence of the other ion possessing in general a different partition coefficient.

Beutner (*loc. cit.*) has studied numerous cells, generally of the type reversible with respect to one ion, e.g. the $\text{Na}^{\cdot}$ in the following:

$$\begin{array}{ccccccccccccccc} \text{Calomel} & \vdots & \text{KCl} & | & \text{Na}X & \| & \text{Na}X & | & \text{NaCl} & \| & \text{NaCl} & | & \text{KCl} & | & \text{Calomel} \\ & \vdots & \text{sat.} & | & \text{in water} & \| & \text{in oil} & | & \text{in oil} & \| & \text{in water} & | & \text{sat.} & | & \\ & & & & & V_1 & & a & & V_2 & & & & & \end{array}$$

or the chlorine ion:

$$\begin{array}{ccccccccccc} \text{Calomel} & | & Y\text{Cl} & \| & Y\text{Cl} & | & \text{NaCl} & \| & \text{NaCl} & | & \text{Calomel} \\ + & | & \text{in water} & \| & \text{in oil} & | & \text{in oil} & \| & \text{in water} & | & - \\ & | & c_1 & V_1 & c_2 & | & c_3 & V_2 & c_4 & | & \\ & & & & & b & & & & & \end{array}$$

In each cell there are two-phase boundaries || giving rise to interphase potentials owing to unequal ionic distribution. The E.M.F. of such a cell is consequently given by the potential

$$V = V_1 - V_2$$

if the small potential differences a or b be neglected.

In the second cell, if the chlorine ion concentrations in the four phases be c_1, c_2, c_3, c_4, we obtain

$$V_1 = \frac{RT}{F} \log \frac{c_2}{c_1} + L,$$

$$V_2 = \frac{RT}{F} \log \frac{c_3}{c_4} + L,$$

$$\therefore\ V = V_1 - V_2 = \frac{RT}{F} \log \frac{c_2\,c_4}{c_1\,c_3}.$$

In one experiment of Beutner, guaiacol was used as immiscible solvent, $\frac{N}{10}$ aniline hydrochloride and $\frac{N}{10}$ sodium chloride as electrolytes, assumed to be completely ionised in aqueous solution. The partition coefficient of these electrolytes in the guaiacol being determined by the increase in the specific conductivity of the solution after shaking with the aqueous electrolytes.

The specific conductivity of the guaiacol before contact was found to be 0·1 gemhos, after contact with the $\frac{N}{10}$ NaCl 1·3 gemhos, an increase of 1·2 gemhos. With $\frac{N}{10}$ aniline hydrochloride, the conductivity rose to 10·3 gemhos. Inserting these values as representative of the concentrations of the chlorine ions in the various solutions, we obtain

$$\frac{c_4}{c_1} = \frac{0{\cdot}1}{0{\cdot}1} = 1,$$

$$\frac{c_2}{c_3} = \frac{10{\cdot}3 - 0{\cdot}1}{1{\cdot}2} = \frac{10{\cdot}2}{1{\cdot}2} = 8{\cdot}5;$$

$$\therefore\ V = 0{\cdot}058 \log 8{\cdot}5 = 0{\cdot}056 \text{ volt},$$

whilst the observed value was found to be 0·059 volt.

A closer agreement is scarcely to be expected since no correction has been made for the concentration potential b and the conductivity ratio of the two solutions is only an approximate measure of the chlorine ion concentrations, which in turn are not identical with their activities.

The following figures indicate the close agreement between the observed and calculated values when various electrolytes are substituted for the aniline hydrochloride. The effect of increasing oil solubility of the cation is clearly marked:

Salt $\frac{M}{10}$ concentration	E.M.F. obs.	E.M.F. calc.
$MgCl_2$	− ·091	− 0·043
KCl	+ ·011	+ 0·012
$C_6H_5NH_3Cl$	+ ·059	+ 0·056
$C_6H_5N(CH_3)_2HCl$	+ ·091	+ 0·100

Various modifications of these cells have been investigated by Beutner (*loc. cit.*), Haber (*loc. cit.*), Cremer (*Zeit. f. Biol.* XLVII. 1, 1906) and others which have many important applications in biology. (Loeb and Beutner, *Biochem. Zeit.* LI. 288, 300, 1913.)

If aqueous solutions containing an electrolyte MX in two different concentrations c_1, c_2 be separated by an oil layer, the maximal voltage of the cell regarded as a concentration cell in respect to one ion will be given by the expression

$$\begin{array}{c|c|c} \text{Water} & \text{Oil} & \text{Water} \\ MX & & MX \\ c_1 & & c_2 \end{array}$$

$$V = \frac{RT}{F} \log \frac{c_1}{c_2},$$

whilst the minimum value will be $V = 0$.

In general the E.M.F. of the cell will be between these values, since the potential difference between the oil-aqueous phases will possess a certain finite value.

If the ionic concentration at the interface to the liquid c_1 be $c_{1,\text{oil}}$ and at c_2 be $c_{2,\text{oil}}$, the potential difference of the cell will be

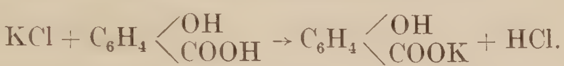
$$V = \frac{RT}{F} \log \frac{c_1}{c_2} \cdot \frac{c_{2,\text{oil}}}{c_{1,\text{oil}}}.$$

When $c_{2,\text{oil}} = c_{1,\text{oil}}$, i.e. when the concentration of the common ion is uniform throughout the whole of the oil, the potential difference is a maximum, whilst when the ions obey the partition law

$$\frac{c_1}{c_{1,\text{oil}}} = \frac{c_2}{c_{2,\text{oil}}},$$

the total E.M.F. is zero.

To establish the conditions of uniform ionic concentration throughout the oil, the ionic concentration of the reversible ion in the oil must be independent of the concentration of the ion in the aqueous phases. Partial realisation of this state of affairs has been obtained by Beutner (*loc. cit.*) utilising salicylaldehyde as non-aqueous phase. The aldehyde contains small quantities of acid which reacts with the potassium chloride



$$KCl + C_6H_4\begin{matrix}/OH\\ \backslash COOH\end{matrix} \rightarrow C_6H_4\begin{matrix}/OH\\ \backslash COOK\end{matrix} + HCl.$$

On solution in the aldehyde the two acids salicylic and hydrochloric are comparable in strength; hence for dilute aqueous solutions of potassium chloride the potassium ion concentration in the aldehyde depends entirely on the quantity of salicylic acid in the salicylaldehyde and the relative strengths of the two acids in this solvent. With more concentrated aqueous solutions the potassium ions present in the aldehyde will be in combination not only with salicylate ions, but with chlorine ions as well, thus promoting an interfacial potential difference. It is to be anticipated that with increasing concentrations of chloride in the aqueous phases the E.M.F. of the cell will gradually fall, an anticipation verified by experiment.

c_1	c_2	Max. E.M.F. calc.	E.M.F. obs.
$\frac{N}{2}$	$\frac{N}{10}$	·041	·021
$\frac{N}{10}$	$\frac{N}{50}$	·041	·025
$\frac{N}{50}$	$\frac{N}{250}$	·041	·034
$\frac{N}{250}$	$\frac{N}{1250}$	·041	·041

If the oil-insoluble chlorine ion be replaced by the oil-soluble salicylate ion in the aqueous phases, the concentration of the electrolyte in the oil phase will not be independent of the concentration in the aqueous phase, but a normal partition coefficient will be obtained with concomitant interphase potential.

Evidently the non-aqueous phase may possess acidic or basic characters either in virtue of its own properties, e.g. nitrobenzene and aniline, or through the addition of small quantities of soluble acidic or basic substances, e.g. salicylic acid to salicylaldehyde or methylamine to nitrobenzene.

It is thus possible to arrange the various non-aqueous media in a series with the aid of a cell of the type

$$\text{Calomel} \left| \begin{array}{c} MX \\ \text{in } H_2O \\ c \end{array} \right| \begin{array}{c} \text{non-aqueous} \\ \text{phase} \\ \text{I} \end{array} \left| \begin{array}{c} \text{non-aqueous} \\ \text{phase} \\ \text{II} \end{array} \right| \begin{array}{c} MX \\ \text{in } H_2O \\ c \end{array} \Big| \text{Calomel}$$

in which the E.M.F. actually measured is the difference in the potentials between the two non-aqueous phases and aqueous solutions containing the same concentration of electrolytes.

Some of the values obtained by Beutner are given below. In all cases normal KCl was used as aqueous phase.

C_6H_5CHO	Cresol	− 0·13 volt
,,	Phenol	+ 0·13 ,,
,,	Guaiacol	+ 0·08 ,,
,,	Acetophenone	− 0·07 ,,

The oil solubility of various ions can be compared one with another by the aid of cells of the type

$$\begin{array}{c} MX \\ \text{in } H_2O \end{array} \Big| \text{ Oil } \Big| \begin{array}{c} MY \\ \text{in } H_2O \end{array} \quad \text{and} \quad \begin{array}{c} MX \\ \text{in } H_2O \end{array} \Big| \text{ Oil } \Big| \begin{array}{c} NX \\ \text{in } H_2O \end{array}$$

Utilising potassium chloride in the left-hand compartment of the cell and substituting for potassium chloride other potassium salts in the right-hand compartment of the cell, the E.M.F. of the cell rises as the anion becomes more oil soluble. Beutner (*Zeit. Elektrochem.* XXIV. 94, 1918) found the following order for increasing oil solubility of the anions:

$$SO_4'' \quad Cl' \quad Br' \quad I' \quad SCN',$$

whilst for increasing oil solubility of the cations the order was

$$Mg^{\cdot\cdot} \quad Ca^{\cdot\cdot} \quad Ba^{\cdot\cdot} \quad Na^{\cdot} \quad K^{\cdot}.$$

The general order was found frequently to be independent of the nature of the oil (Baur, *Zeit. Elektrochem.* XXIV. 100, 1918), especially in those cases where the oil possessed distinct acidic or basic characters.

The study of bioelectrical phenomena (see *Bull. Nat. Research Council*, No. 69, May, 1929) indicates that potential differences of considerable magnitude exist across the membranes of living cells, and it is natural to attempt to construct some type of artificial cell which will reproduce these conditions. It cannot be said that any definite conclusion has been arrived at in the matter; whilst the condition of equilibrium between the contents of a blood cell and its serum are defined by the Donnan equilibrium, yet selective permeability has to be attributed to the membrane. Such selective powers we have seen are possessed under certain conditions, not only by a sieve membrane but also by a homogeneous membrane (see Ch. IX). The properties of artificial membranes prepared from gelatine and casein (see p. 353) and also from albumin and globulin (Matsuo, *Pflüg. Archiv*, CC. 132, 1923; Höber, *Zeit. physikal. Chem.* CX. 142, 1924; Mond, *R. Arch. ges. Physiol.* CCIII. 247, 1924), which on account of their heterogeneity must be regarded as sieve membranes, have led many to believe that living membranes behave in like manner. We must observe that such a membrane with different solutions on each side of it cannot be regarded as containing a uniform gel, since the properties of a gel change with its environment. On the other hand the effect of organic lipoid solvents on the membrane as well as the ease of penetration of lipoid soluble materials show clearly that the membrane is at least composite in character and that bioelectric potentials might arise across a lipoid aqueous phase interface as imagined by Beutner. It would be of great interest to examine the properties of a composite membrane consisting of two lipoid layers enclosing an aqueous ampholytic protein layer in a search for an interpretation of many of the phenomena observed with living cells.

13. The glass electrode.

Haber and Klemenziewicz (*Zeit. physikal. Chem.* LXVII. 385, 1909) showed that if two solutions of different P_H, into each of which a calomel electrode dips, are separated by a thin glass membrane an E.M.F. is obtained equal to $\frac{RT}{F}$ × the difference in P_{H}. The glass is evidently to be considered as a solid electrolyte containing $\mathrm{H}^{\cdot}$ and OH' ions at a constant thermodynamic potential which depends only on the electrical potential of the glass, as that of the mercurous ions in mercury depends only on the electrical potential of the mercury, whilst the thermodynamic potential in the aqueous phase is a function of the concentration. Hence

$$dV = \frac{d\mu_{\mathrm{H}^{\cdot}}}{96{\cdot}5 \times 10^{10}}.$$

The behaviour of the glass electrode has been examined in more detail by a number of investigators, notably Meyer (*Wied. Ann.* XL. 244, 1890), Borelius (*Ann. de Phys.* XLV. 929, 1914), Freundlich and Rona (*Sitz. Preuss. Akad. der Wiss.* 397, 1920), ibid. and Ettisch (*Zeit. physikal. Chem.* CXVI. 401, 1925), Hughes (*J.A.C.S.* XLIV. 2860, 1922), Horovitz (*Zeit. f. Physik.* XV. 368, 1923), Cremer (*Zeit. f. Biol.* XXIX. 562, 1908; *Zeit. physikal. Chem.* CXV. 424, 1925).

It is found that in alkaline solutions ($P_{\mathrm{H}} > 11$ for soft glass) the glass no longer functions as a hydrogen electrode, but is affected by an alteration in the sodium ion concentration of the solution. With sodium amalgams, in fact, glass may serve as a sodium electrode of constant thermodynamic potential.

In addition to hydrogen and sodium ions other metallic ions such as silver may be present in glasses which thus act as mixed electrodes. When equilibrium is attained between all the electromotively active ions in the glass and solution the formal relationship

$$V = \frac{RT \log C_{\mathrm{H}^{\cdot}} - K_{\mathrm{g.\,H}^{\cdot}} - K_{\mathrm{l.\,H}^{\cdot}}}{96{\cdot}5 \times 10^{10}} = \frac{RT \log C_{\mathrm{Na}^{\cdot}} - K_{\mathrm{g.\,Na}^{\cdot}} - K_{\mathrm{l.\,Na}^{\cdot}}}{96{\cdot}5 \times 10^{10}}$$

must be obeyed.

It follows that the thermodynamic potentials of the hydrogen and sodium ions in the glass must be affected by the concentrations in the solution, or ionic replacement in the glass occurs. This power of ionic interchange is shared in common with glass by the naturally occurring hydrated silicates, e.g. the zeolites.

CHAPTER VIII

CONDITIONS OF STABILITY IN SUSPENSIONS AND EMULSIONS

In discussing the various methods by which dispersions such as suspensions or emulsions are formed, we noted that the stability of such systems was not necessarily determined by the fact that they could be prepared. An examination of the dispersion by means of a microscope, or if the dispersion be a fine one, an ultramicroscope, reveals the fact that the small particles are in a state of lively agitation—the Brownian movement. Impact between various particles would necessarily follow from such thermal agitation and if such impact permitted the agglomeration of the particles, resulting in a decrease in the free surface energy of the system, precipitation or coagulation would ensue. In general, however, such suspensions and emulsions are stable, and some factor must necessarily be operative either in preventing coalescence on collision or in reducing the number of collisions. The chief factor to be considered is the electrical charge on the suspensions and emulsions. We have already noted that electrification may result either by a process of superficial ionisation or by preferential adsorption of an ion in solution. The disperse phase is thus charged and the particles may be regarded as somewhat massive ions. On discharging the particles the forces opposing coalescence on collision are removed and coagulation results. In this chapter we shall consider the nature of the Brownian movement and the mechanism by which the charge on the particles may be reduced by various means so as to effect coagulation and precipitation.

1. The Brownian movement.

In the seventeenth century Leeuwenhoek first noted that microscopic animalculae when suspended in water were not at rest but were in a state of rapid agitation. Nevertheless, until the investigations of Robert Brown (*Edin. Phil. Jour.* v. 358, 1828; *Phil. Mag.* IV. 161, 1828; VI. 161, 1829; VIII. 41, 1830), these movements were always associated with the ciliary agitation of living organisms. Brown, however, examined fine suspensions of inert materials such as finely divided metals, wax, coal and many other substances, and confirmed the existence of this irregular motion as a general property of fine suspensions. He likewise proved that this agitation was not caused by convectional currents in the liquid nor by disturbances which might be produced by evaporation. Experiments on the Brownian movement of small particles in liquids were continued and extended by Wiener (*Pogg. Ann.* CXVIII. 79, 1863), F. Exner (*Wien. Sitz. Ber. Natur. Wiss.* LVI. 116, 1867), Dancer (*Trans. Manc. Phil. Soc.* 162, 1868), Jevons (*ibid.* 78, 1870), Cantori (*Nuovo Cimento*, XXVII. 156, 1867) and others without success in the elucidation of the cause of the motion. That the Brownian agitation was the result of molecular bombardment was suspected by Carbonelle in 1874, Deslaux (*J. Roy. Microscopic Soc.* 1877) and by Bodaszewski (*Chem. Centralblat*, XVII. 709, 1881), who first observed similar irregular zigzag motions in the particles of smoke from burning paper and in the fog particles of ammonium chloride, but this point of view was first stated in a definite form by Gouy (*J. de Physique*, VII. 561, 1881; *C.R.* CIX. 102, 1889) and Ramsay (*Chem. News*, LXV. 90, 1892).

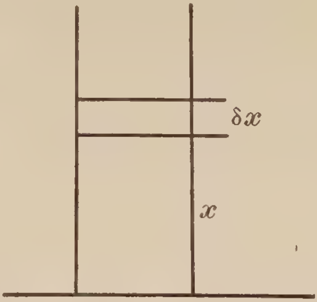
That the Brownian agitation could be regarded as nothing less than a visible proof of the kinetic theory and that the small suspended particles could be regarded for this purpose as large and visible molecules was confirmed and elaborated by the experimental work of Zsigmondy, F. Exner, Henri, Chaudesaignes, and Perrin. These investigators showed that the motions of the small particles were in experimental agreement with those that would be anticipated from an application of the kinetic theory, making the basic assumption that the suspended particle may be regarded for kinetic purposes as a large molecule possessing a mean kinetic energy equal to the mean kinetic energy of a molecule of the solution in which it is suspended, the theoretical application of which has been extended in detail by Perrin, A. Einstein and v. Smoluchowski.

Such a conception does not necessarily carry with it the implication that the particle possesses a true molecular weight.

2. The distribution of particles in colloidal suspensions.

In a vertical cylinder of liquid containing a suspension slightly denser than the surrounding liquid in which it is dispersed we should anticipate that since the suspension particles behave exactly in the manner which large molecules might be expected to behave when equilibrium is attained, the suspension density would be greatest at the bottom of the cylinder and least at the top, establishing an exponential concentration gradient similar to the atmosphere around the globe. The following conditions of equilibrium were established by Perrin (*Les Atomes*).

Consider the equilibrium in a vertical cylinder of suspension of density ρ_1 in a suspension medium of density ρ_2 of unit cross-section and height x_0. If at a height x there are n particles per unit volume and at a height $x + \delta x$, $n + \delta n$ particles per unit volume, the difference in osmotic pressures due to the particles on the assumption that the suspension conforms to the laws of an ideal solution will be



$$\frac{RT}{N} n - \frac{RT}{N} (n + \delta n) \quad \text{or} \quad -\frac{RT}{N} \delta n.$$

This difference in osmotic pressures at equilibrium exactly balances the apparent weight due to gravitational attraction of the particles in this small volume of unit cross-section. The number in the cross-section is $n \delta x$ and if V be the volume of each particle the apparent weight of the particles will be

$$n \delta x \,.\, V (\rho_1 - \rho_2) g.$$

Thus at equilibrium we obtain

$$-\frac{RT}{N} \delta n = - n \delta x \, V (\rho_1 - \rho_2) g,$$

or

$$\frac{RT}{N} \log \frac{n}{n_0} = V (\rho_1 - \rho_2) g (x - x_0),$$

where n and n_0 are the number of particles per unit volume at heights x and x_0 respectively.

Perrin tested this relationship with particles of gamboge and mastic dispersed in water. Gamboge emulsions are readily prepared by rubbing gamboge with a soft brush under water or by solution in alcohol and pouring rapidly into a large excess of water. The emulsions thus prepared contain particles of varying sizes, but by submission to a process of fractional centrifuging an emulsion of spherical particles reasonably uniform in diameter may be prepared.

The mean density of the emulsion particles was determined both from the specific gravity of the solid and from the specific gravity of an emulsion containing a known amount of the solid in the dispersed state; no effect due to dispersion on the apparent density could be detected.

The determination of the volume of the individual particles in the case of gamboge was effected by three different methods.

(*a*) By observation of the rate of fall of the upper surface of a dilute emulsion in a capillary tube maintained at a constant temperature the limiting velocity of fall of the particles can be determined.

According to Stokes the limiting velocity v imparted to a sphere moving through a liquid of viscosity η under a constant applied force F is given by

$$v = \frac{F}{6\pi\eta r},$$

where r is the radius of the sphere. In the case of the spherical gamboge emulsions settling under the influence of gravity

$$F = \frac{4}{3}\pi r^3 (\rho_1 - \rho_2) g,$$

or

$$r = \sqrt{\frac{9}{2}\frac{\eta v}{(\rho_1 - \rho_2) g}}.$$

Although Stokes' law does not apply to particles so small that the Brownian movement influences the rate of gravitational settling, yet for the relatively coarse emulsions prepared in this way no sensible error is introduced.

(*b*) On acidulating a gamboge emulsion the particles are rapidly precipitated. By precipitating the particles from a known volume on to a glass coverslip the number originally contained in the volume could readily be counted with the aid of a low power microscope. From a knowledge of the total quantity of gamboge in the emulsion and the number of particles present, the individual volume can readily be ascertained.

(*c*) By precipitating a sufficient number of gamboge particles on a glass coverslip the length of a string of particles could be measured and the number in the string counted, from which the radius could be deduced.

As typical of the variations in particle radius determined by these three methods the following experimental values of Perrin for gamboge emulsions may be cited:

Method	$r \times 10^{-4}$ cm.		
	(*a*)	(*b*)	(*c*)
Emulsion I	·49	—	·50
„ II	·45	·46	·46
„ III	·3675	·3667	·371
„ IV	·213	·212	—
„ V	·15	·14	—

The distribution of particles in a vertical column of the emulsion was determined by Perrin with the aid of a microscope and micrometer focusing arrangement. The height of the column under the microscope was 0·1 mm. and the number at various depths was counted with the aid of the eye. The following results are typical of such determinations.

(i) Radius of gamboge particle $2{\cdot}6 \times 10^{-5}$ cm.:

Depth increment	0	6 μ	12 μ	18 μ
Number	305	530	940	1880
Calculated number	280	528	995	(1880)

(ii) Radius of gamboge particle $1{\cdot}06 \times 10^{-5}$ cm.:

Depth increment	0	30 μ	60 μ	90 μ
Number	12	22·6	47	100
Calculated number	11·1	23	48	(100)

The difficulty associated with such a conception of an atmospheric concentration gradient applicable to colloidal particles is that with the rate of increase observed by Perrin over a depth of 0·1 mm. the concentration at a depth of say 1 cm. would already be enormous. In actual practice, however, the concentration has been found to approach a limiting value, and to become virtually constant after a definite maximum has been reached. This fact has led to a criticism of Perrin's work by Burton (*Proc. Roy. Soc.* A, C. 705, 1922). Burton ascribes this discrepancy to the fact that the particles are charged and consequently exert a mutual repulsion on one another. He suggests that this charge on the particles will exert a force on a unit charge equivalent to $kn\epsilon$ in the layer δx, consequently the total force on the layer of particles in the thickness δx will be $(kn\epsilon)(n\epsilon\delta x)$ or $kn^2\epsilon^2\delta x$.

Perrin's equation will thus be modified by the inclusion of this term to

$$\frac{RT}{N}\,\delta n + kn^2\epsilon^2\delta x = n\,\delta x\,V\,(\rho_1 - \rho_2)\,g.$$

Writing this in the form $A\delta n = (Cn - Bn^2)\,\delta x$, we obtain

$$n = \frac{C}{B + ke^{-\frac{C}{A}x}}.$$

Thus for large values of x, n becomes constant and equal to

$$\frac{C}{B} = \frac{V\,(\rho_1 - \rho_2)\,g}{ke^2}.$$

Porter and Hedges (*Trans. Farad. Soc.* XVIII. 1, 1922) criticise Burton's treatment by pointing out that the colloidal solution does not in fact contain charges all of one sign but is electrically neutral as a whole; further, that a charged colloidal particle with its attached double layer should at small distances function as an electrical doublet and thus not repel but actually attract other and similar doublets. They point out that the extension of Perrin's treatment to great depths is only possible if we replace the simple Van t' Hoff law $\pi = cRT$ obtaining in dilute solutions by the osmotic laws of concentrated solutions.

Porter makes use of the Sackur-Porter osmotic law for concentrated solutions

$$\pi = \frac{nRT}{N(1-bn)},$$

where b corresponds to the b term in Van der Waals' equation and is proportional to the volume of the osmotically active particle together with its water of solvation, thus

$$\frac{d\pi}{dn} = \frac{RT}{N(1-bn)^2} \quad \text{.....................(1).}$$

If the osmotic pressure be a function of the hydrostatic pressure of the solution p and of the numerical concentration, we have the mathematical identity

$$\frac{d\pi}{dp} = \left(\frac{d\pi}{dp}\right)_n + \left(\frac{d\pi}{dn}\right)_p \cdot \frac{dn}{dx}\frac{dx}{dp}.$$

Porter has shown (*Trans. Farad. Soc.* XIII. 123, 1917; *Proc. Roy. Soc.* A, LI. 522, 1917) $\frac{d\pi}{dp} = \frac{\rho_2 - s}{\rho_2}$, where s is the shrinkage. Also

$$\frac{d\pi}{dp} = 1 - \frac{dp_0}{dp} = \frac{u-\sigma}{u}, \quad \text{also} \quad \frac{dp}{dx} = \frac{g}{\sigma},$$

where σ is the specific volume of the solution, u that of the solvent.

Hence
$$\frac{s-\sigma}{u} = \frac{\sigma}{g} \cdot \frac{d\pi}{dn}\frac{dn}{dx} \quad \text{.....................(2).}$$

From (1) and (2) we obtain

$$\frac{dn}{dx} = \frac{s-\sigma}{u\sigma}\frac{gN}{RT}(1-bn)^2.$$

If there be no contraction when gamboge and water are intermingled $\sigma = c\rho_1 + (1-c)u$, where ρ_1 is the density of gamboge and $s = u$.

$$\therefore\ s - \sigma = c(\rho_1 - u) = nm(\rho_1 - u),$$

thus
$$\frac{dn}{dx} = kn(1-bn)^2,$$

where
$$k = \frac{gNm(\rho_1 - u)}{RTu^2},$$

or
$$\log_e \frac{n}{1-bn} + \frac{1}{1-bn} = kx + A.$$

This curve tends asymptotically for large values of x to the value $n_\infty = \frac{1}{b}$ and has a point of inflection for $n = \frac{n_\infty}{3}$.

The following experimental values were obtained by Porter:

x in cm.	·023	·033	·043	·063	·083	·103	·123	·143
$n \times 10^{-6}$	·95	2·14	3·61	7·14	8·69	9·52	9·76	9·76

whilst values calculated with the aid of the above equation were, putting $b = 10{\cdot}2 \times 10^{-8}$ cm.^{3}, $k = 121$,

x in cm.	·024	·032	·0375	·047	·061	·089	·115
$n \times 10^{-6}$	1	2	3	5	7	9	9·7

3. The Brownian movement of translation.

According to Stokes' law the limiting velocity of a spherical particle of radius r moving through a liquid of viscosity η under the influence of a force F is

$$v = \frac{F}{6\pi\eta r}.$$

If there are n particles in a unit volume of liquid, then $\frac{nF}{6\pi\eta r}$ will move through a sq. cm. per second.

The force acting on a particle suspended in a solution will be caused by the osmotic pressure differences in the suspension or

$$Fn = \frac{d\pi}{dx},$$

but for dilute solutions $\pi = \frac{RTn}{N}$ or $\delta\pi = \frac{RT\,\delta n}{N}$,

hence
$$\frac{nF}{6\pi\eta r} = \frac{RT\,\delta n}{N\,\delta x\,.\,6\pi\eta r}.$$

If we denote the diffusion coefficient of the particles by D, the quantity moving across unit area under the influence of a concentration gradient $\frac{dn}{dx}$ will be $D\frac{dn}{dx}$.

The quantity moved by diffusion will be that impelled by the difference in osmotic pressure, or

$$D\frac{dn}{dx} = \frac{RT\,\delta n}{N\,.\,6\pi\eta r\,\delta x},$$

or

$$D = \frac{RT}{6\pi\eta r N},$$

giving us a value for the diffusion constant in terms of the temperature and viscosity of the medium and the radius of the particle. For very small particles Stokes' law is no longer exact and the departure to be expected with decreasing diameter has been investigated in some detail by Sutherland (*Phil. Mag.* VI. 1, 781, 1905), Cunningham (*Proc. Roy. Soc.* A, LXXXIII. 357, 1910), and Millikan (*Phys. Rev.* XXXII. 349, 1911).

Of the various formulae suggested, that proposed by Cunningham appears to conform most closely to Millikan's experimental values. We obtain

$$D = \frac{RT}{N\,.\,6\pi\eta r}\left(1 + A\frac{\lambda}{r}\right),$$

where A is a constant $= 0{\cdot}815$ and λ the mean free path of a molecule of the solvent.

Einstein (*loc. cit.*) showed further that the actual mean distance $\bar{x}$ travelled by a particle in a short time t under the influence of random molecular collisions was related to the diffusion constant D by the following equation:

$$\bar{x}^2 = 2Dt \quad \text{or} \quad \bar{x}^2 = \frac{R}{N}\frac{Tt}{3\pi\eta r}.$$

Langevin (*C.R.* CXLVI. 530, 1908) has obtained this relationship in a relatively simple manner.

If we consider a particle of mass m moving parallel to the x axis with a component velocity $\dot{x}$ under the influence of molecular shocks, the equation of motion will be

$$m\ddot{x} = -6\pi\eta r\dot{x} + \phi,$$

where ϕ is the force due to molecular collision, which is constantly varying both in magnitude and sign but nevertheless impels the particle continuously.

Then
$$\tfrac{1}{2}m\frac{d^2x^2}{dt^2} - m\dot{x}^2 = -3\pi\eta r\frac{dx^2}{dt} + \phi x.$$

For a large number of identical particles the term ϕx vanishes. Replacing $\frac{dx^2}{dt}$ by z, we obtain

$$\frac{mdz}{2dt} + 3\pi\eta r z = m\dot{x}^2.$$

Now $\frac{1}{2}m\dot{x}^2$ is the mean kinetic energy of the particle due to the component of its velocity parallel to the x axes, or

$$m\dot{x}^2 = \frac{RT}{N} \quad \text{and} \quad \frac{mdz}{2dt} + 3\pi\eta r z = \frac{RT}{N}.$$

The solution of the equation is

$$z = \frac{RT}{N\,.\,3\pi\eta r} + Ce^{-\frac{6\pi\eta r}{m}t}.$$

When the motion reaches a steady state

$$z = \frac{RT}{N\,.\,3\pi\eta r},$$

from which by integration we obtain

$$\bar{x}^2 = \frac{R}{N}\,\frac{Tt}{3\pi\eta r}.$$

Independently of Einstein, v. Smoluchowski arrived at a similar solution to the problem of the mean displacement of a particle. He obtained

$$\bar{x}^2 = \frac{32}{27}\,\frac{R}{N}\,\frac{Tt}{3\pi\eta r}.$$

4. The Brownian motion of rotation.

Not only do particles in Brownian agitation move rapidly about in the suspension medium, the magnitude of the movements being capable of exact calculation from the foregoing mathematical considerations, but they are likewise undergoing rotational motion due to an unequal distribution of molecular impacts upon the faces of the parts of the particle on each side of its axis of rotation.

The mean energy of rotation will necessarily by the laws of equipartition of energy be equal to the mean energy of translation.

Einstein (*loc. cit.*) has shown that the mobility of a system (B) referred to a parameter a is related to the mean displacement δ by the following equation

$$\delta^2 = \frac{2R}{N}\,Tt\,.\,B,$$

where t is the time in which the alteration δ in the parameter a due to molecular bombardment has taken place.

In the case of translational motion $B = \frac{1}{6\pi\eta r}$ or $\bar{x}^2 = \frac{RTt}{N.3\pi\eta r}$.

In the case of rotational motion, if a torque of moment I be applied to a sphere of radius r in a medium of viscosity η, the angular velocity acquired by the sphere (see v. Kirchhoff, *Vorlesungen über Mechanik*, 26) will be $\dot{\omega} = \frac{I}{8\pi\eta r^3}$.

Hence $$B = \frac{1}{8\pi\eta r^3}.$$

Thus $$\bar{r}^2 = \frac{RTt}{N \cdot 4\pi\eta r^3},$$

where r is the angle of rotation.

5. Fluctuations in concentration.

As has already been indicated, a dilute disperse system may be regarded as obeying the ordinary gas laws. If we imagine a small volume of the disperse system as separated from the bulk of the solution, it will contain at any instant a certain number of particles n. Since these particles are agitated by Brownian movement, the number of particles in the small volume will alter from moment to moment but always maintaining a mean value of n over long periods of time. If at any instant the number in the small volume be n_i, then the relative alteration from the mean value n will be

$$\delta = \frac{n_i - n}{n}.$$

Or the mean value of these fluctuations in concentration will be

$$\bar{\delta} = \left(\frac{n_i - n}{n}\right)_{\text{mean}}.$$

v. Smoluchowski has shown, on the assumption of the validity of Boyle's law for such suspensions, that

$$\bar{\delta} = \sqrt{\frac{2}{\pi n}}$$

when n is large, and when n is small

$$\bar{\delta} = \frac{2n^k e^{-n}}{k!},$$

where k is the next smallest whole number when n is not a whole number, and is equal to n when n is a whole number.

If Boyle's law does not hold exactly, the above equations suffer the following transformations.

For large values of n, $\bar{\delta} = \sqrt{\frac{2}{\pi n} \cdot \frac{\beta}{\beta_0}}$; for small values of n,

$$\bar{\delta} = \frac{2n^k e^{-n}}{k!} \sqrt{\frac{\beta}{\beta_0}}, \text{ where } \frac{\beta}{\beta_0} = \frac{RT}{v^2\left(\frac{RT}{[v-b]^2} - \frac{2a}{v^3}\right)}.$$

The probability of the presence of n_i molecules being present inside the small element of volume will be

$$\frac{n^{n_i} e^{-n}}{n_i!}.$$

6. Experimental verification.

On the assumption that the particles of a suspension diffuse at a rate dependent on the concentration gradient in the solution in a manner analogous to the molecules of a soluble solute, the diffusion coefficient is given by the expression

$$D = \frac{RT}{6\pi \eta r N}.$$

This relationship permits of experimental verification by direct observation of the diffusion coefficient and the measurement of the radius of the particle. Svedberg (*Zeit. physikal. Chem.* LXVII. 105, 1907; *Archiv f. Kemi. etc., K. Svenska Vetensk. Akad. Stockholm*, B, IV. 12, 1911) employed colloidal gold prepared by reduction with phosphorus according to the directions of Faraday and Zsigmondy.

The density of the water employed as diffusion medium was raised by the addition of urea in order that the gold suspension could be run under a column of water without undue disturbance so as to obtain a uniform level surface of separation.

As a result of a series of experiments the following results were obtained.

T	η	Δ obs.	r calc. in $\mu\mu$	r obs. (by Zsigmondy)
(i) 284·7	0·012	0·27	0·6	*ca.* 0·5
(ii) 286·62	0·01209	0·117	1·29	1·33 (direct observation)

If the motion of one particle be observed it will oscillate about a mean position, the actual motion being naturally zigzag, returning after a comparatively long time interval very nearly to its original position. The determination of the displacement of a particle in a given time interval will thus vary with the interval chosen; from the relationship

$$\bar{x}^2 = \frac{RT}{N \, . \, 3\pi\eta r} t$$

the velocities for different time intervals will evidently increase as the time interval diminishes and at a rate proportional to the inverse square root of the time interval or $v^2 t =$ constant.

Likewise the displacement in a given time interval, i.e. for constant values of t, should vary both as $\frac{1}{\sqrt{r}}$ and $\sqrt{\frac{T}{\eta}}$.

Confirmation of these expected relationships have been obtained by Chaudesaignes (*C.R.* CXLVII. 1044, 1908), Perrin, Exner, and others.

With gamboge particles $1{\cdot}065 \times 10^{-5}$ cm. in radius, it was found by examination of the motion of fifty particles at thirty second intervals that each moved on the average:

in	30	seconds	6·7	microns
„	60	„	9·3	„
„	90	„	11·8	„
„	120	„	13·95	„

whilst the square roots of the times are proportional to the numbers 6·7, 9·46, 11·6 and 13·4.

Svedberg obtained the following values for the displacement of gold particles over varying time periods, confirming the anticipated relationship $\bar{x} = \kappa\sqrt{t}$.

(*a*)

t in secs.	$\bar{x}$ in μ	$\bar{x}$ in μ calc.
1	1·2	—
2	1·6	1·7
3	2·0	2·0
4	2·4	2·4
5	2·5	2·8

(*b*)

t in secs.	$\bar{x}$ obs.	$\bar{x}$ calc.
1	4·0	—
2	5·4	5·7
3	6·2	6·9
4	7·8	8·0

For particles of a radius $r = 22\mu\mu$ the absolute displacements were calculated by the aid of Einstein's equation and compared with those determined by the aid of the ultramicroscope. He obtained

t in secs.	$\bar{x}$ in μ calc.	$\bar{x}$ in μ obs.	Difference
1	4·3	4·1	+ 0·2
2	5·8	5·8	—
3	6·6	7·6	− 1·0
4	8·3	8·2	+ 0·1

By observing the velocities of particles of radii 5×10^{-5} and $2·13 \times 10^{-5}$ cms. respectively for equal time intervals, the square of the velocities were found to vary inversely as the radii; thus with a thirty second time interval the following data were obtained:

t	$r \times 10^5$ cms.	$\bar{x}$ calc.	$\bar{x}$ obs.
30 seconds	2·13	3·4	3·6
	5·00	1·56	1·55

By determination of the velocities of particles in water at various temperatures, Exner (*loc. cit.*) was able to show the dependence of the velocity on the temperature and viscosity of the medium he found:

t	$r \times 10^5$ cms.	$T°$ C.	η	$\bar{x}$
0·14 second	4·5	21	·01	33·0
		71	·004	51·0

whence $\sqrt{\frac{T_1}{\eta_1}} : \sqrt{\frac{T_2}{\eta_2}} :: 1 : 1·7$ and $\bar{x}_1 : \bar{x}_2 :: 1 : 1·6$.

These experiments have been extended and confirmed by Seddig with the aid of a microphotographic camera to the case of suspensions of cinnabar (*Phys. Zeit.* IX. 465, 1908).

Svedberg (*Die Existenz der Molekule*, Leipzig, 1912) employed as observational method a thin flat cell through which the colloidal solution was run at a slow and known rate. The particles viewed through a micrometer eyepiece are seen as curves of light moving with a given amplitude A and wave length λ. All the particles, however, cannot be regarded as possessing a motion of a purely oscillating character about the axis of the flowing stream, and thus Svedberg's method of examination of the displacements $\bar{x}$ in given time intervals is liable to be somewhat inaccurate. Nevertheless, as the following data indicate, good agreement between the experimental figures and the theoretical expectations was obtained.

Dispersion medium	Platinum particles $r = 25\,\mu\mu$				
	T° C.	$\eta \times 10^3$	A in μ	$t \times 10^3$ secs.	$\frac{A^2\eta}{t}$
Acetone ...	18	3·2	6·2	16	7·8
Ethyl alcohol	19	4·6	3·9	14	5·04
Amyl acetate	18	5·9	2·9	13	3·74
Water	20	10·2	2·1	0·65	6·72
n-Propyl alcohol	20	22·6	1·3	0·45	8·9

It will be noted that the value of the expression $\frac{A^2\eta}{t}$ is approximately constant.

Gold Suspension.

No. of particles per $384\,\mu^3 = 1{\cdot}4$.

n_i	Fractional frequency of occurrence		
	Obs.	Calc.	Difference
0	0·07	0·02	+ 0·05
1	0·08	0·08	0
2	0·11	0·16	− 0·05
3	0·13	0·20	− 0·07
4	0·23	0·20	+ 0·03
5	0·19	0·15	+ 0·04
6	0·12	0·09	+ 0·03
7	0·04	0·05	− 0·01
8	0·02	0·02	0
9	0·01	0·01	0

$$n = 3{\cdot}81$$

$$\frac{n_i - n}{n} = 0{\cdot}418$$

$$\frac{2n^k e^{-n}}{k!} = 0{\cdot}408$$

$$\frac{\beta}{\beta_0} = 1{\cdot}024$$

In Einstein's formula $\overline{x} = 4A$, hence the anticipated dependence of A^2 on the viscosity and time of amplitude is amply confirmed by experiment.

MERCURY SUSPENSION.

No. of particles per 384 μ^3 = 0·5.

	Fractional frequency of occurrence		
n_i	Obs.	Calc.	Difference
0	0·07	0·05	+ 0·02
1	0·15	0·15	0
2	0·21	0·23	− 0·02
3	0·21	0·22	− 0·01
4	0·16	0·17	− 0·01
5	0·11	0·10	+ 0·01
6	0·04	0·05	− 0·01
7	0·04	0·02	+ 0·02
8	0·01	0·01	0

$$n = 2{\cdot}99$$

$$\frac{n_i - n}{n} = 0{\cdot}479$$

$$\frac{2n^k e^{-n}}{k\,!} = 0{\cdot}450$$

$$\frac{\beta}{\beta_0} = 1{\cdot}134$$

Svedberg has likewise examined v. Smoluchowski's equation for the fluctuation in concentration of suspensions with the time, experimentally with the aid of a Siedentopf-Zsigmondy ultramicroscope. Two suspensions were employed, one a gold suspension of mean particle radius 29$\mu\mu$, the other one of mercury of mean particle radius 71$\mu\mu$. The data given above are typical of the results obtained.

7. Electrolytic coagulation.

It has been noted that for substances which do not yield ions in solution, such as charcoal, the charge is always produced by the preferential adsorption of an ion from the solution, e.g. the hydrogen ion. For substances which yield ions in solution, e.g. the hydroxides, it is evident that the charge can be accounted for by superficial ionisation (see Zsigmondy, *Kolloidchemie*; Wolfgang-Pauli, *Trans. Farad. Soc.* XVI. 6, 1921), e.g.:

$$\{Fe\,(OH)_3\}_x \rightarrow \{Fe\,(OH)_{3\,(x-1)}\,Fe\,(OH)_2\}^+ + OH',$$

or $$\{H_2SiO_3\}_z \rightarrow \{(H_2SiO_3)_{z-1}HSiO_3\}' + H^{\cdot}.$$

In some cases also the charge may be attributed to the entrainment of impurities in the substance during its preparation; thus in the formation of arsenious sulphide from the oxide and hydrogen sulphide there is little doubt that the colloidal arsenious sulphide contains hydrogen sulphide which undergoing partial ionisation results in the formation of a negatively charged colloid

$$\left\{\begin{matrix}As_2S_{3x}\,H_2S\\ H_2O\end{matrix}\right\} \rightarrow \left\{\begin{matrix}As_2S_{3(x-1)}\,H_2SHS\\ H_2O\end{matrix}\right\}' + H^{\cdot} \rightarrow \left[\begin{matrix}As_2S_{3(x-1)}\,H_2S\\ H_2O\,.\,S\end{matrix}\right]'' + 2H^{\cdot}.$$

The coagulation and eventual precipitation of colloidal suspensions by electrolytes are the result of a series of reactions which in general cannot be isolated one from the other.

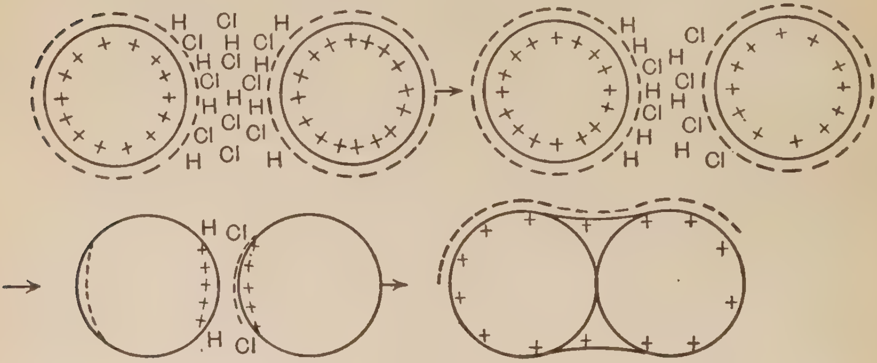
Coagulation, the result of approach, contact and coalescence of the particles of the suspensoid, is evidently hindered by any factor which may retard one of these three actions. The approach of one particle to another is brought about by the thermal or Brownian movement of the particles within the medium, and factors such as low temperature, high viscosity of the medium or large particle size will evidently diminish the rate of approach. When the particles are in close proximity to one another, actual contact will be prevented if the particles possess electric charges similar in sign, due to the action of electrostatic repulsion. The particles will possess no net charge, i.e. their surface will be covered with the same number of cations and anions, and will not repel one another at the isoelectric point when the capillary attraction can operate effectively (Hardy, *Proc. Roy. Soc.* A, LXVI. 110, 1900).

Actual electrostatic attraction may indeed take place between particles at the isoelectric point by processes which can be represented diagrammatically, as follows.

If the electric double layer is to some extent movable over the surface of the particle, we may imagine at the isoelectric point the effect of the mutual approach of two particles possessing each an equal number of cations and anions, e.g. $H^{\cdot}$ and Cl', in which the cations are most readily adsorbed in the diagram on p. 384.

The normal distribution of ions in the double layer will be altered; in one particle the anions may be drawn to the exterior of the double layer, in the other the cations; the ions of opposite sign will move away, and the sides of the two particles in close proximity to one another will thus exhibit opposite polarity.

On the assumption of a somewhat mobile double layer, electrostatic attraction between particles may occur, due to this displacement effect, even if the total net charge be not zero, i.e. coagulation may take place before the isoelectric point is reached. The data of Zsigmondy on gold particles, and of Powis (*Zeit. physikal. Chem.* LXXXIX. 186, 1915) on oil particles, have indeed shown that the optimum point for precipitation is not actually at the isoelectric point, although in the case of gold practically complete discharge of the double layer had to take place before coalescence.



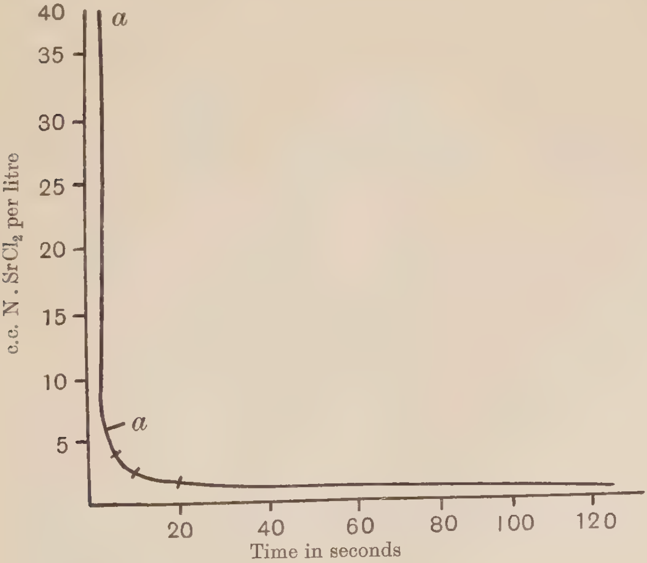
Powis found in the case of oil emulsions, that a relatively large electrokinetic potential, $\zeta = 0{\cdot}040$ volt, did not prevent coagulation, an indication that the surface adsorbed layer is more mobile than for gold.

In addition to electric charge between particles, other factors are in some cases operative in preventing actual contact; thus the medium may be strongly adsorbed by the surface, and the thin film may not readily be displaced on collision of the two neutral particles; in other cases a tough elastic film may be formed, possessing definite mechanical strength and necessitating a violent impact to ensure rupture.

Coalescence does not immediately follow after contact. Zsigmondy has noted, in the case of gold sols, under the ultramicroscope, that the small primary particles coalesce on contact to form secondary particles, that a primary will coalesce with a secondary, but two secondary particles do not coalesce.

The primary action of an electrolyte in the coagulation of a suspension is that of adsorption which is governed by the rate of diffusion. Subsequently the discharged or partially discharged primary particles coalesce, the colloid becomes more coarse, the secondary particles grow in number, and finally the colloid flocculates. If a coagulating electrolyte be added to a suspension in increasing concentrations, the velocity of aggregation first rises rapidly with the concentration, and then more slowly to a maximum value. At this concentration we may assume that on every approach of two neutral particles to within a certain critical distance coalescence occurs, but in more dilute solutions only a certain fraction of the approaches are operative in producing coalescence.

The following curve obtained by Zsigmondy (*Kolloidchemie*, III. p. 67) on the effect of strontium chloride of different concentrations on the rate of conversion of a red into a blue colloidal gold, indicates clearly the two regions of coagulation, one for high concentrations of electrolyte where the rate of precipitation is



practically independent of the concentration, and the other where, as has already been mentioned, every collision is not effective in producing coagulation and the rate of precipitation is greatly affected by the concentration of the added electrolyte.

Zsigmondy noted that the time of coagulation in the region of high concentrations (*a–a*) was not only independent of the concentration but also of the nature of the added electrolyte, being, for the particular gold sol investigated, a period of from 5 to 7 seconds. In this region we must assume that every collision between primary particles results in adherence, and the rate of adherence will thus be dependent on the magnitude of the Brownian movement causing the particles to diffuse within one another's spheres of attraction. v. Smoluchowski (*Physikal. Zeit.* XVII. 587, 1916; *Zeit. physikal. Chem.* XCII. 129, 1917) has calculated the rate of coagulation of a sol taking into consideration that not only do the primary amicrons but the secondary, tertiary and those particles of a higher state of aggregation continue to increase during the process.

If P_0 be the number of primary particles originally present in the sol and after a time t there be P_1, P_2, P_3 primary, secondary and tertiary particles present, v. Smoluchowski showed that

$$\Sigma P = P_1 + P_2 + P_3 = \frac{P_0}{1+\beta t},$$

where $\beta = 8\pi P_0 D r$ in which $D =$ the diffusion coefficient and r the radius of the particle ($2r$ being taken as the mean distance apart of two particles when within one another's sphere of attraction).

Also
$$P_1 = \frac{P_0}{(1+\beta t)^2},$$

$$P_2 = \frac{P_0 \beta t}{(1+\beta t)^3},$$

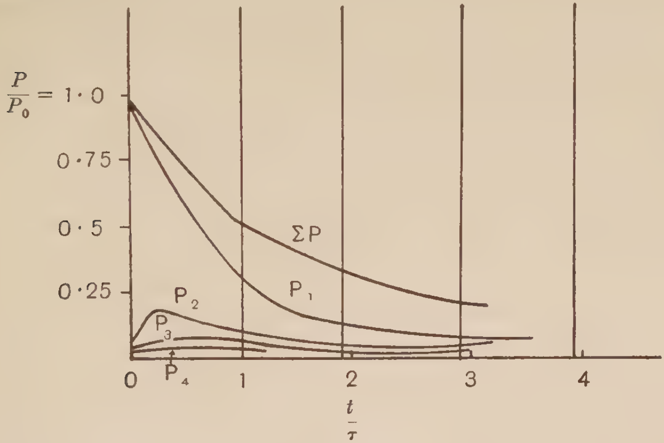
$$P_n = \frac{P_0 (\beta t)^{n-1}}{(1+\beta t)^{n+1}}.$$

The half life of the suspension, i.e. the period which must elapse for the total number of particles to be reduced by coagulation to one-half, the primary particles being simultaneously reduced to one-quarter of their original number, is given by

$$\tau = \frac{1}{\beta} = \frac{1}{8\pi D r P_0}.$$

With the aid of the above expressions the number of particles of various complexities present in the solution after a time t expressed as a fraction or multiple of the half life τ can readily be calculated; these are graphed in the following curves.

v. Smoluchowski's formula has been tested both by an examination of the rate of decrease of the primary particles present in a gold suspension undergoing coagulation and also by counting the rate of decrease of the total number of particles in similar suspensions.



The data given overleaf were obtained by Zsigmondy (*Zeit. physikal. Chem.* XCII. 600, 1918) for the rate of decrease of primary particles in a gold suspension undergoing coagulation.

The mean radius of the sphere of action around each particle calculated from the observed rate of coagulation is $31{\cdot}82 \times 10^{-7}$ cm. or some one and a quarter times the actual radius of the particle.

Similar results have been obtained by Westgren and Reitstötter (*Zeit. physikal. Chem.* XCII. 750, 1918) with gold suspensions somewhat coarser than those employed by Zsigmondy and by

Kruyt and v. Arkel (*Rec. d. Trav. Chim. d. Pays-Bas*, XXXIX. 656, 1920) for selenium.

$P_0 = 0{\cdot}27 \times 10^{10}$; radius of particle $24{\cdot}2 \times 10^{-7}$ cm.

t secs.	P_1 obs. (relative value)	$\frac{\beta}{2}$	P_1 calc.
0	1·97	—	1·97
3	1·56	(0·040)	1·76
20	1·02	0·0195	1·04
40	0·66	0·0183	0·64
40	0·76	(0·0153)	0·64
60	0·44	0·0187	0·44
80	0·49 (?)	(0·0126)	0·31

In the following table is given the rate of decrease of the total number of particles of a gold suspension undergoing coagulation:

t secs.	$\Sigma P \times 10^{-8}$	β calc.
0	2·69	—
60	2·34	0·149
120	2·25	0·098
240	2·02	0·083
420	1·69	0·083
600	1·47	0·083
900	1·36	0·065
1370	1·20	0·057

On the addition of small quantities of electrolyte all the amicrons are not discharged by ionic adsorption. Only those that are completely discharged or those for which the electrokinetic potential has been reduced below the critical maximum will actually adhere to one another on contact. We should thus with v. Smoluchowski (*loc. cit.*) replace the half life period $\tau = \dfrac{1}{8\pi D r P_0}$ by an expression $\tau = \dfrac{1}{8\pi D r P_0 x}$, where x is the number of successful collisions.

This expression for the slow coagulation has in fact been confirmed by Westgren (*Arkiv för Kemi, Min. och Geol.* VII. 1918) for coarse gold suspensions, but the investigations by Paine

(*Kolloidchem. Beihefte*, IV. 24, 1912) on copper suspensions; Miyazawa (*J.C.S.* Tokio, XXXIII. 1179, 1912), Ishizaka (*Zeit. physikal. Chem.* LXXXIII. 97, 1913; LXXXV. 398, 1913) and Gann (*Kolloidchem. Beihefte*, VIII. 65, 1916) on aluminium hydroxide, and Lottermoser (*Koll. Zeit.* XV. 145, 1914) on tungstic acid, and Wiegner (*Koll. Zeit.* VIII. 227, 1911) and Galecki (*Zeit. anorg. Chem.* LXXIV. 174, 1912) on gold, have shown that the rate of coagulation over the sensitive range of electrolyte concentration is not a simple reaction of the first order as postulated by the above considerations but behaves as if the reaction were autocatalytic in that the reaction velocity of coagulation can be expressed by means of an expression of the type

$$\frac{dx}{dt} = k(1 + bx)(1 - x).$$

As an example the following data obtained by Gann (*loc. cit.*) on the flocculation of an aluminium hydroxide sol with potassium chloride (60 millimols KCl per litre) may be cited.

t min.	η	x	k
0	52·4	—	—
2	52·4	—	—
5	52·4	—	—
10	52·4	—	—
15	52·6	·0172	(·0017)
22	52·8	·0345	(·0018)
30	53·0	·0517	·0021
40	53·3	·0776	·0022
50	53·7	·1120	·0021
60	54·1	·1465	·0023
75	54·5	·1810	·0023
90	55·1	·2328	·0023
105	55·6	·2758	·0024
120	56·2	·3275	·0024
140	57·0	·3966	·0024
160	57·8	·4655	—
	$\eta_\infty = 64·0$		

The rate of coagulation of night blue examined by Biltz and Steiner (*Zeit. physikal. Chem.* LXXIII. 507, 1910) and of benzopurpurin (Biltz and v. Vegesack, *Zeit. physikal. Chem.* LXXIII. 500, 1910) likewise appear to conform reasonably closely to a reaction of the autocatalytic variety.

No satisfactory explanation for the autocatalytic behaviour of the flocculating suspension has as yet been advanced. The rates of coagulation have been determined in a variety of different ways, by ultramicroscopic counting in the case of gold, by alterations in the viscosity in the case of aluminium hydroxide, by the amount of precipitate separating in given times for the copper, and the increase in light scattering in the case of tungstic oxide. That all should indicate an autocatalytic action would appear to preclude any error being introduced by the methods employed for ascertaining the rate; we are thus forced to conclude that large particles formed by the aggregation of numerous amicrons act as nuclei on which further aggregation can occur more readily than on amicrons or small aggregates. When the suspension under examination is in motion the quantity of liquid streaming past and in the sphere of influence of a large aggregate will naturally be greater than that flowing past a smaller particle, and thus the number of possible contacts between the amicrons in the streaming liquid and the particles will increase rapidly with the size of the particle. This possible mode of mechanism for the autocatalytic nature of the process has been suggested by v. Smoluchowski (*Zeit. physikal. Chem.* XCII. 155, 1917). Apart from such mechanical effects, however, it would seem possible that the alteration in the electrokinetic potential of the aggregate on growth would lead to such an autocatalytic action as observed. We have already noted that coagulation may occur when this potential fall is not zero but slightly greater. If we imagine a particle with the critical electrokinetic potential it can only coalesce with an uncharged amicron. If the original charge be e and the radius of the particle r the potential of the particle will be $\frac{e}{Kr}$, where K is the S.I.C. of the medium. After coalescence the effective volume of the particle will be larger and its intrinsic potential consequently reduced to $\frac{e}{Kr'}$, where r' is obtained from the relationship

$$\tfrac{4}{3}\pi r'^3 = \tfrac{4}{3}\pi (r^3 + r_0^3).$$

If the diminution in intrinsic potential is accompanied by a corresponding decrease in the electrokinetic potential, the new aggregate will now not be at the critical point but will be able to coalesce with another particle which possesses a slight electrokinetic potential. Thus aggregates will be built up which can react more readily than the small ones owing to a decrease in the interfacial potentials.

8. The adsorption and entrainment of ions.

Colloidal suspensions and emulsions acquire their charge owing to preferential adsorption of cations or anions, thus a negative suspension or emulsion will be precipitated on the addition of an electrolyte containing a readily adsorbable cation; the added electrolyte however contains an anion as well, and tends to counteract the effect of the cation, hence the amounts of various electrolytes containing a common cation necessary to produce coagulation will vary with the nature of the anion, as is instanced by the following data on the minimal amounts of electrolytes necessary to precipitate identical quantities of the same suspension.

Colloid	Sign	Minimal precipitating concentrations in millimols per litre	
Platinum	−	NaCl 2·5	NaOH 130·00
$Fe(OH)_3$	+	HCl 4·00	$BaCl_2$ 9·64

In the former case the sodium is the precipitating ion, in the latter the chloride; it is evident however that the hydroxyl ion is more readily adsorbed by the platinum than the chloride, necessitating a greatly increased concentration of the sodium hydroxide to effect precipitation.

A suspension or emulsion acquiring a positive charge owing to selective adsorption of a positive ion, e.g. $H^{\bullet}$ ion, will leave in the surrounding medium in the double layer an equal and opposite charge, e.g. a chloride ion; on the addition of a fresh electrolyte possessing a more readily adsorbable anion, e.g. Na_2SO_4, a reaction will occur:

$$\overbrace{\text{Colloid } 2H^{\bullet} + 2Cl'} + 2Na^{\bullet} + SO_4'' \rightarrow \overbrace{\text{Colloid } 2H^{\bullet}SO_4''} + 2Na^{\bullet} + 2Cl'.$$

The suspension or emulsion will be coagulated and the coagulum or precipitate will contain the coagulating anion in amount necessary to give the original suspension electric neutrality.

Crum (*Ann. Chim. Pharm.* LXXXIX. 156, 1854), analysing the coagulum produced by the addition of electrolytes to aluminium hydroxide, showed that the acid or salt necessary for coagulation was always present. Linder and Picton (*loc. cit.*) in their investigations on the precipitating power of various cations on the negative arsenious sulphide suspension showed that the precipitate always contained the cation, but never the anion of the precipitating electrolyte, e.g. $Ba^{\cdot\cdot}$, on the addition of barium chloride.

Whitney and Ober (*J.A.C.S.* XXIII. 824, 1901) on careful analysis of these precipitates found that the amounts of positive ions entrained were proportional to their electrochemical equivalents, as indicated by the following table:

Ion	Mgrm. ions adsorbed by 100 c.c. As_2S_3 sol	
	obs.	calc.
Ba	7·6	(7·6)
Ca	2·0	2·2
Sr	3·9	4·9
K	3·6	4·3

The precipitate on analysis gave the ratio Ba : 90 As_2S_3. The constancy of the ratio however depends entirely on the size and charge of the arsenious sulphide particles, since the reaction proceeds to the isoelectric point, i.e. electrical neutrality, and is therefore independent of any definite stoichiometric ratio of reactants.

Gann (*Kolloidchem. Beihefte*, VIII. 127, 1916) has likewise measured the adsorption of various precipitating anions by colloidal aluminium hydroxide and found that, although the liminal concentrations necessary for precipitation are very different, yet precipitation is caused on adsorption of equivalent concentrations as indicated by the following figures.

Anion	Liminal concentration millimols per litre	Adsorbed quantity in milli-equivalents
Salicylate	8·00	0·30
Picrate ...	4·00	0·18
Oxalate ...	0·36	0·36
Ferricyanide	0·10	0·27
Ferrocyanide	0·08	0·29

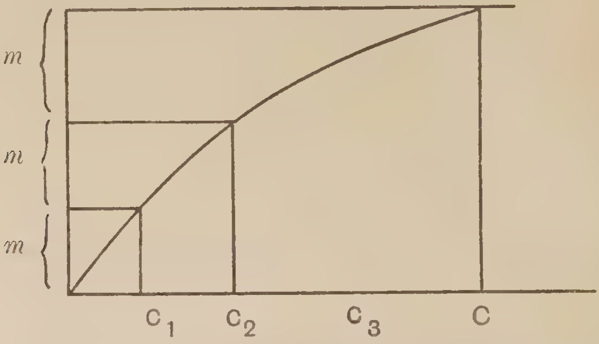
Similar investigations by Sen (*Biochem. Zeit.* CLXIX. 193, 1926) have shown, as is to be anticipated, that as in general both ions are adsorbed the precipitate analysis cannot conform strictly to the equivalent rule since this refers only to the excess adsorption of the precipitating ion.

Rabinowitsch and Kargin (*Zeit. physikal. Chem.* CXXXIII. 203, 1928) conclude from potentiometric measurements that, on the addition of a coagulating salt such as sodium sulphate to a ferric hydroxide chlorine ion containing sol, prior to coagulation chlorine ions are displaced from the colloid by the sulphate ion, and the composition of such a sol is accordingly $[\{Fe(OH)_3\}_n \{Fe(Cl)_3\}_m Fe(OH)_2]^+ Cl'$, the chlorine ion constituent of the particle being first replaced by SO_4'' ions on the addition of the electrolyte.

In the adsorption of a monovalent, divalent and trivalent ion the amounts adsorbed to produce electrical neutrality will stand in the ratio $3m : 2m : m$, whilst if the adsorption is assumed to follow the Freundlich isotherm the bulk concentrations C_1, C_2, C_3 necessary to produce precipitation will evidently follow no regular order, but be dependent on the variables a and n of the isotherm expression. Thus on the addition of aluminium chloride to arsenious sulphide some 50–60 % of the aluminium ions are adsorbed, whilst with monovalent cations only about 1 % is adsorbed.

Freundlich (*Kapillarchemie*, pp. 150–151; *Zeit. physikal. Chem.* LXXIII. 404, 1910) assumes that different ions are equally adsorbed at equal electrical concentrations. In the light of more recent investigation this assumption has been shown to be perfectly unwarranted.

In some cases adsorption of the ion resulting in precipitation may promote apparent hydrolysis, as instanced in the case of charcoal (p. 275); thus if gum mastic suspension in water, a negative colloid, be floated on a solution of copper sulphate the copper ions will be adsorbed and the solution will be left feebly acid—a phenomenon noted by Spring (*Rec. Trav. Chim. Pays-Bas*, IV. 215, 1900).



The replacement of a positive ion in a negative colloid by another positive higher valent ion more readily adsorbable may result in electric neutralisation and consequent precipitation. Thus Duclaux (*J.P.C.* v. 1, 23; *C.R.* CLIV. 1426, 1912) noted that negative suspensions of copper ferrocyanide prepared from the potassium salt always contained potassium and were precipitated in the usual way by other positive ions, e.g. $H^{\cdot}$, $Ba^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$; the potassium ion however could afterwards be detected in the medium, indicating a replacement by the more readily adsorbed ion. The potassium was originally probably not part of the original complex ferrocyanide molecule, but adsorbed by the suspension from the solution. A similar displacement effect has been noticed by Pauli and Matula (*Koll. Zeit.* XXI. 49, 1917) in the case of sulphate ions displacing the less adsorbable chloride ions on ferric oxide.

9. Lyotropic series.

In the adsorption of electrolytes by charcoal it was noted that the organic ions were strongly adsorbed; in decreasing order of adsorptive power the hydrogen and hydroxyl followed by the other cations and anions in a regular series. The factors determining the position of the ion in this, the lyotropic series, were primarily the valency, and secondly its electropositive nature and mobility. The phenomenon of coagulation of suspensions gives a rough indication of the degree of adsorption of a particular ion, and the coagulation concentrations of various electrolytes for suspensions has been the object of many systematic investigations, notably by Schulze (*J. f. prakt. Chem.* XXV. 431, 1883; XXVII. 370, 1883; XXXII. 390, 1884), Linder and Picton (*J.C.S.* LXI. LXVII. LXXI.), Freundlich (*Zeit. physikal. Chem.* LXXIII. LXXIX. LXXX. LXXXIII. LXXXV. LXXXVI.), Whetham (*Phil. Mag.* XLVIII. 474, 1899), Hardy (*J. of Physiol.* XXXIII. 258, 1905) and others.

10. The valency rule of precipitation.

The effect of valency on precipitatory power is most marked, the polyvalent ions being much more effective than the monovalent ions. As a rough approximation the liminal concentrations, i.e. the concentrations in milligram ions per litre necessary to cause coagulation, vary with the valency in the proportion Valency 1 : 2 : 3, coagulative concentrations $1:\frac{1}{x}:\frac{1}{x^2}$, where x is a constant approximately 30. The coagulative powers, i.e. the reciprocal of the coagulative concentrations of mono-, di-, and tri-valent ions, should thus stand in the ratio 1 : 30 : 900. The following ratios represent the averages of a number of readings by the various investigators:

Freundlich	1 : 104 : 810
Linder and Picton	1 : 63 : 863
Schulze	1 : 49 : 810

Evidently the valency relationship is by no means rigid, and in addition the various observations do not agree amongst themselves. It has already been noted that the process of coagulation is the result of a series of independent operations primarily dependent on an adsorptive process due to diffusion; the manner in which the experiments are conducted thus affects the liminal concentrations observed. The addition of a strong solution of an electrolyte to a dilute suspension will produce local precipitation, whereas the addition of large quantities of dilute electrolyte to a concentrated suspension will not produce any effect, although the final dilutions may be identical.

Again, it is extremely difficult to define precipitation. Small quantities of electrolyte will produce coalescence of the ultramicrons and the amicrons, producing a coarser suspension before actual precipitation occurs; this again may only be partial.

The following method of comparing the precipitatory power of electrolytes has been found to give very uniform results.

The dilutions of electrolytes are so arranged that equal volumes of solution are added to equal volumes of the dispersion. The addition is performed rapidly, e.g. by adding 10 c.c. of electrolyte to 10 c.c. of suspension in test tubes. After thorough admixture the time elapsing to produce a standard degree of coarseness in the dispersion is noted. The standard can conveniently be made by the addition of small quantities of electrolyte and allowing the suspension to stand overnight. The degree of coarseness of the control is immaterial, provided precipitation does not take place. The concentration-time curves of various electrolytes can readily be compared in this manner.

Burton and Bishop (*J.P.C.* June, 1922) and Kruyt (*Koll. Zeit.* XXII. 81, 1918; *Rec. Trav. Chim. Pays-Bas*, XXXIX. 656, 1920; XL. 249, 1921) have found that the ratio electrolyte : colloid is not the only governing factor in the production of coagulation; this ratio varies with the actual concentration of the suspension employed, and appears to obey a regular rule, which may be formulated as follows.

The ionic concentration necessary to produce coagulation varies with increasing concentration of the suspension; with monovalent ions the ratio electrolyte : suspension necessary increases, with trivalent ions it decreases, with divalent ions the ratio appears to be independent of the concentration.

The valency of the precipitating ion is however not the only factor operative, as is tacitly assumed in the law of precipitation already discussed. This fact is clearly brought out in the order of adsorption of various ions on the surface of charcoal. A glance at the table indicates that in a definite series, such as the alkali metals or the halides (Pappada, *Koll. Zeit.* IV. 56, 1909) the electropositive nature of the element is an important factor.

We note also the influence of the solubility of the product formed by interaction of the precipitating ion with the surface of the colloid in the following data presented by Freundlich for the precipitation of mercuric sulphide.

Salt	$AgNO_3$	$HgNO_3$	$TlNO_3$	$CuSO_4$	$HgCl_2$
Liminal concentration millimols/litre	0·44	0·071	0·14	0·047	0·11
Salt	$Pb(NO_3)_2$	NaCl	KCl	$BaBr_2$	$Ce(NO_3)_3$
Liminal concentration millimols/litre	0·35	13·0	10·0	0·68	0·056

11. Ionic mobility and adsorbing power.

There exists also a relationship between the adsorbing power and the ionic mobility, a point developed by Mukherjee (*Trans. Farad. Soc.* XVI. 103, 1921) embracing the following assumptions.

An ion adsorbed on the surface of a suspension will draw near to it an ion of opposite sign in the solution; these ions in the double layer are thus bound and can only escape if their kinetic energy exceeds a definite critical value W. If the chemically adsorbed ions have a valency n_1 and n_2 is the valency of the opposite charged ions in the liquid of dielectric constant K in contact with the solid and separated from the former by a distance δ, we obtain

$$W = \frac{n_1 n_2 \epsilon^2}{\delta K} \quad \text{..........................(i),}$$

where ϵ is the electronic charge.

The probability of an ion remaining fixed is given by $1 - e^{-\frac{W}{kT}}$, where k is the Boltzmann gas constant $= 1{\cdot}372 \times 10^{-16}$ erg/degree, T the absolute temperature. There will thus be at any definite temperature a number of free ions and ions bound to the double layer; the free ions will, as it were, form a second sheet in the double layer.

On the assumption that the double layer is of the order of 1 Å. (see p. 316) thick with a surface charge of 1 to 2×10^4 C.G.S. units, equivalent to 10^{13} monovalent ions per sq. cm., the mean distance between the ions is 3×10^{-6} cms., a distance extremely great compared with molecular dimensions. Mukherjee assumes in consequence that the neighbouring ions have but comparatively little effect on an oppositely charged ion at its position of minimum electrical energy.

The maximum amount of an ion of opposite sign that can be adsorbed per unit area is equivalent to the charge per unit area. If we denote the number adsorbed of valency n_1 by N, the maximum number of opposite sign that can be adsorbed N_m of valency n_2 is expressed by the relationship

$$N_m n_2 = N n_1 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(ii)}.$$

If we denote by θ_1 the fraction of this maximum adsorbed when equilibrium has been reached in presence of ions of opposite sign in solution having a concentration c, then the rate of evaporation of these adsorbed ions must be equal to the number readsorbed in the same time. The rate of evaporation per unit surface is evidently

$$K_1 \theta_1 N_m e^{-\frac{W}{kT}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(iii)},$$

where K_1 is a constant and $N_m \theta_1$ the number of ions adsorbed per unit surface. The rate of adsorption depends on two factors: (*a*) the rate of collision of oppositely charged ions and (*b*) the number of places where adsorption is possible, that is, the spaces left by the free ions. This is given by

$$N - N_m \theta_1 = N\left(1 - \frac{n_1}{n_2}\theta_1\right) \ldots\ldots\ldots\ldots\ldots\text{(iv)}.$$

The rate of collision (*a*) is determined by the rate of diffusion of the ions to the surface, and by the electrostatic attraction between the ions. The former is equivalent to the action of a force equal to $\frac{RT}{N_0}$, whilst the intensity of the electrical field is proportional to the density of the charge on the surface and equal to

$$K_2' (1 - \theta_1)\, n_1 N n_2 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\text{(v)}.$$

Since N and n_1 are constants for the same surface we may write this expression as $K_2 (1 - \theta_1)\, n$, where K_2 is a constant. In comparison with the enormous electrostatic field the diffusive force is negligible. Under these conditions the rate of collision is given by

$$K_3(1-\theta_1)CUn_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(vi)},$$

where C is the ionic concentration in the liquid in contact with the surface and U the ionic mobility. The rate of adsorption, being proportional to the rate of collision and the spaces available, from equations (iv) and (vi) is given by

$$K_4\left\{N\left(1-\frac{n_1}{n_2}\theta_1\right)\right\}\{(1-\theta_1)CUn_2\}.$$

Finally for equilibrium we obtain the relationship

$$K_1\theta_1 N_m e^{-\frac{W}{kT}} = K_4 N\left(1-\frac{n_1}{n_2}\theta_1\right)(1-\theta_1)n_2 CU.$$

Since N, n_2, k and $e^{-\frac{W}{kT}}$ are constants for the same ion we obtain

$$\theta_1 = \kappa\frac{n_2}{n_1}C\left(1-\frac{n_1}{n_2}\theta_1\right)(1-\theta_1) \quad \ldots\ldots\ldots\ldots\ldots(a),$$

where $$\kappa = \frac{K_4}{K_1}n_2 U e^{-\frac{W}{kT}}.$$

Likewise for the fraction of the original charge not neutralised by adsorption we have $$\theta_2 = 1-\theta_1 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(b).$$

Evidently the electrical adsorbability of an ion of opposite charge is dependent on the product nU or its valency and its mobility. Thus for a negative surface Mukherjee gives the following order of adsorption:

$$\text{Th} > \text{Al} > \text{Ba} > \text{Sr} > \text{Ca} > \text{Mg} > \text{H} > \text{Cs} > \text{Rb} > \text{K} > \text{Na} > \text{Li}$$

forming a lyotropic series, whilst for the anions the order should be

$$\text{Br} > \text{NO}_3 > \text{SCN} >$$
$$\text{CO}_3 > \text{SO}_4 > \text{OH} > \text{I} > \text{Cl} > \text{COOH} > \text{F}.$$

Mukherjee has extended his hypothesis to a consideration of the effects of electrolytes on electric endosmose, utilising the data of Elissafoff (*Zeit. physikal. Chem.* LXXIX. 385, 1912) (see p. 325).

On the assumption that at a glass-electrolyte interface hydroxyl ions are adsorbed, the fraction of the original charge neutralised by adsorption can be calculated from the above equations as follows. From (*a*) and (*b*)

$$\theta_1 = \kappa \frac{n_2}{n_1} C \left(1 - \frac{n_1}{n_2}\theta_1\right)(1-\theta_1),$$

$$1 - \theta_2 = \kappa \frac{n_2}{n_1} C \left(\frac{n_2 - n_1}{n_2} + \frac{n_1}{n_2}\theta_2\right)\theta_2$$

$$= \left(\kappa C \frac{n_2 - n_1}{n_1}\right)\theta_2 + \kappa C \theta_2{}^2,$$

or

$$\kappa C \theta_2{}^2 + \theta_2 \left(\kappa C \frac{n_2 - n_1}{n_1} + 1\right) - 1 = 0.$$

For hydroxyl ions $n_1 = 1$ and putting $n_2 = 1$ for the adsorption of an oppositely charged monovalent ion we have

$$\kappa C \theta_2{}^2 + \theta_2 - 1 = 0.$$

For a divalent ion

$$\kappa C \theta_2{}^2 + \theta_2 (\kappa C + 1) - 1 = 0.$$

The following data calculated with the aid of these equations show a remarkably close agreement with those calculated by Elissafoff.

Electrolyte NaCl, $k = \cdot 0076$.

Glass capillary concentration 10^{-6} grm. ion per litre	$50\theta_2$ obs.	$50\theta_2$ calc.
22·5	43	43·4
68·0	37	36·4
136·0	31	30·6
225·0	26	26·4
2240·0	8	10·6
4500·0	5	7·8

Electrolyte $BaCl_2$, $k = \cdot 0163$.

Glass capillary concentration 10^{-6} grm. ion per litre	$50\theta_2$ obs.	$50\theta_2$ calc.
2·2	47	46·7
4·4	46	44·0
6·0	41	42·0
22·0	28	31·5
110·0	15	15·0

The two factors of valency and ionic mobility are however not the only ones to be considered in the phenomenon of adsorption, since the lyotropic series developed from these considerations alone should remain invariable in all cases of coagulation. This is far from being the case; the order varies in a marked manner with the nature of the suspension. In addition, no adequate explanation of the abnormal position of the organic ions is forthcoming on this hypothesis. Bancroft (*Second Report on Colloid Chemistry*, p. 10, 1918; *Applied Colloid Chemistry*, p. 215) has made a careful summary of the series in order of precipitation, as observed by numerous investigators, which clearly indicate that chemical factors characteristic of suspension and electrolyte cannot be ignored. The following may be cited:

Colloid	*Order*	*Reference*
Sulphur ...	Ba Sr > Ca > Al > Mg Cs > Rb > K > Ni Cd Zn > Na > NH_4 > Li > H	Odén, *Der Kolloide Schwefel*, CLVI. 1912
Platinum ...	Al Pb > Ba > Ag > K Na	Freundlich, *Kapillarchem.* p. 352, 1909
Silver ...	Al > Ba > Sr > Ca > H > Cs > Rb > K > na > Li	Pappada, *Bay. Chim. Ital.* XLII. 1, 263, 1912
Mastic ...	Al > Hg_2 > H > Ba Ca > Mg > Ag > nu	Freundlich, *Kapillarchem.* p. 368, 1907
Prussian Blue	Fe Al Cr > Ba Cd > Sr Ca > H > Cs > Rb > K > Na > Li	Pappada, *Koll. Zeit.* IX. 136, 1911
Hydrous ferric oxide	H > Ba > Mg > Li Na K	Pappada, IX. 233, 1911
Albumen ...	Th > Cu Zn > Ca > Mg > Li > K Na > NH_4	

Similar wide variations are found in the case of the anions when precipitating positive suspensions.

As an example of the great precipitating powers of the organic cations the following data given by Freundlich for the precipitation of colloidal arsenious sulphide are of interest.

Electrolyte	Liminal concentration millimols. per litre
NaCl	51·0
Guanidine nitrate ...	16·4
Strychnine nitrate ...	8·0
Aniline hydrochloride...	2·52
Morphine hydrochloride	0·425
Neo-fuchsine	0·114

12. Sign reversal in suspensions.

There exists an equilibrium at the interface between a charged suspension and its solution consisting of a dynamic interchange of both cation and anion. If the suspension be positively charged the adsorption of the positive ion is greater than that of the negative at that particular concentration. On application of the Freundlich isotherm equation to each ion

$$x_c = a c_c^{\frac{1}{n}},$$

$$x_a = a' c_a^{\frac{1}{m}},$$

it is evident that if n and m are not identical on altering the concentration of the electrolyte, the amounts adsorbed of each ion will vary, thus permitting a change in the interfacial potential fall to take place. Bancroft (*Second Report*, p. 2) cites as example the addition of potassium bromide to silver nitrate. If one adds to a dilute solution of silver nitrate somewhat less than one equivalent of potassium bromide a colloidal solution of silver bromide with a positive charge is obtained, having adsorbed an excess of silver ions, and to a less extent of potassium ions over the nitrate ions in the solution. On adding exactly one equivalent the colloid is unstable, since the interfacial potential fall is small; a slight excess of the potassium bromide results in the formation of a negatively charged colloidal solution of the silver bromide due to the adsorption of an excess of bromide ions and to a less extent of nitrate ions over the potassium ions in solution. On increasing the concentration of the potassium bromide the adsorption of the potassium ions eventually equals the adsorption of the anions and precipitation ensues.

The diminution of electrokinetic potential and eventual reversal produced by the addition of electrolytes is more marked in the case of the polyvalent ions, and has been carefully investigated by Burton (*The Physical Properties of Colloidal Solutions*, pp. 164–169) who in the case of a colloidal solution of copper obtained the following results:

Electrolyte	grm. ions per c.c. × 10^6	Mobility at 15° C. × 10^5	Electrolyte	grm. ions per c.c. × 10^6	Mobility at 18° C. × 10^5
KCl ...	0	+ 24·9	K_3PO_4 ...	0	+ 25·4
	17·0	+ 25·7		3·6	+ 21·5
	38·0	+ 26·2		7·2	+ 16·8
	74·0	+ 22·8		14·4	+ 3·4
	154·0	+ 18·7		21·6	− 4·8
				32·8	− 7·9
K_2SO_4 ...	0	+ 25·4	$K_3Fe(CN)_4$	0	+ 30·4
	7·7	+ 25·3		7·1	+ 14·0
	19·2	+ 24·0		14·3	+ 3·8
	38·4	+ 21·8		21·4	+ 1·0
	96·0	+ 14·4		28·6	− 1·5
	153·0	+ 0		42·8	− 9·1

13. Effect of non-electrolytes on suspensions.

Quincke noted (*Drude Ann.* VII. 57, 1902) that both chloroform and carbon disulphide rapidly effected the precipitation of china clay suspensions, an observation extended by Rona and Györgi (*Biochem. Zeit.* XCVIII. 92, 1919) to many capillary active substances such as camphor and thymol. A similar precipitation by ethyl alcohol on platinum and charcoal suspensions has been observed by Billiter (*Zeit. physiol. Chem.* XLV. 312, 1903) and Lehmann (*ibid.* XIV. 151, 1894), whilst W. Ostwald (*Grundriss der Kolloidchemie*, 471, 1909) noted that a silver suspension in water was precipitated on the addition of propyl alcohol. In general however although the addition of non-electrolytes to suspensions does not produce precipitation or coagulation yet the sensitiveness of the sols to precipitation by electrolytes is affected.

The alteration in sensitiveness of a suspension to electrolytes by the addition of a non-electrolyte was first noted by Blake (*Amer. J. of Sci.* XVI. 439, 1903) who observed that the quantity of potassium alum necessary to convert a red gold into a violet form had to be increased on the addition of ether to the suspension; the liminal concentration without ether was found to be ·00035 whilst in an aqueous solution saturated with ether ·00151 equivalent per litre was required.

Kruyt and van Duin (*Kolloidchemie Beihefte*, V. 269, 1914) have examined the alteration in sensitiveness to electrolytes of a suspension of arsenious sulphide to which various non-electrolytes had been added. They found that the influence of various non-electrolytes on the sensitiveness of the suspension ran parallel to the adsorption of the non-electrolytes from aqueous solution by powdered charcoal and that the most capillary active non-electrolyte exerted the greatest effect on the liminal concentration required for precipitation. Further it was observed that the addition of non-electrolytes lowered the liminal concentrations, i.e. increased the sensitiveness of the suspension to mono- and trivalent ions but increased the liminal concentrations, i.e. decreased the sensitiveness for divalent and tetravalent cations as will be noted from the following tables.

Isoamyl alcohol conc. millimols per litre	Liminal concentrations of KCl	Ratio
0	53·5	—
44	48	0·90
66	46	0·86
88	42	0·79

Isoamyl alcohol conc. millimols per litre	Liminal concentrations of $BaCl_2$	Ratio
0	1·075	—
66	1·16	1·01
78	1·32	1·23
92	1·38	1·27

Ethyl alcohol		Ratio
0	0·87	—
1560	0·97	1·12

For a ferric hydroxide suspension they obtained an increase in sensitivity on the addition of both isoamyl alcohol and phenol to both monovalent and divalent anions, whilst Freundlich and Rona (*Biochem. Zeit.* LXXXI. 87, 1917) have noted similar effects on this suspension on the addition of many other capillary active non-electrolytes such as the urethanes, camphor and thymol.

No general explanation for the effect of such non-electrolytes on the sensitiveness of the suspension is as yet forthcoming. It

Electrolytes	Liminal concentrations for water	Isoamyl alcohol concentration	Liminal concentrations	Ratio
KCl	53·5	88	42·0	0·79
NaCl	69·0	85	51·0	0·74
KNO_3	62·0	85	48·0	0·77
$\frac{1}{2}Na_2SO_4$	78·0	85	56·0	0·72
$BaCl_2$	1·07	92	1·38	1·29
$MgSO_4$	1·16	85	1·39	1·20
$ZnSO_4$	1·12	85	1·40	1·25
$AlK(SO_4)_2$	0·203	85	0·177	0·87
$\frac{1}{2}Al_2(SO_4)_3$	0·166	85	0·149	0·90
$Th(NO_3)_4$	0·147	85	0·152	1·03
p-Chlor-aniline chloride	2·18	85	1·93	0·89
Benzidine nitrate ...	0·200	85	0·195	0·98

is evident from the experimental data that the non-electrolyte is adsorbed by the particles and the sensitiveness is affected by such adsorption. W. Ostwald (*loc. cit.*) pointed out that the effect of adsorption of a non-electrolyte of low specific inductive capacity would be to lower the potential of the charged particle and thus a smaller adsorption of the precipitating ion would suffice to bring the potential within the region necessary for coagulation. Freundlich (p. 638) has noted that if this hypothesis be correct then since the cataphoric mobility of the particle is given by the expression

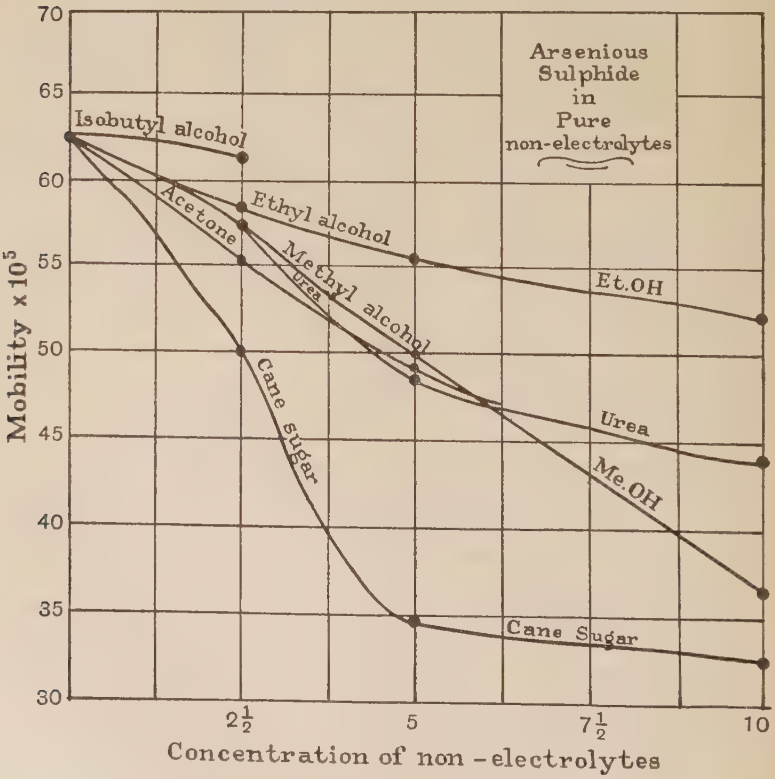
$$u = \frac{\xi H K}{4x\eta}$$

a decrease in the value of K should be associated with a diminution in the velocity of cataphoresis. The following values were obtained for a ferric hydroxide sol on the addition of varying amounts of camphor and thymol.

	$u \times 10^4$ in cms. per sec., for 1 volt per cm.
Pure sol	0·4
5 millimols per litre camphor	0·2
2·5 ,, ,, thymol	0·3

Although an alteration in the specific inductive capacity of the double layer may be effected by the selective adsorption of the non-electrolyte yet such an explanation is evidently by no means adequate; thus we find 1500 millimols of ethyl alcohol as effective as 70 millimols of isoamyl alcohol, whilst the dielectric capacities of water and the two alcohols stand in the ratio 81 : 20·8 : 5·7; again the anomalous behaviour of di- and tetravalent cations as noted by Kruyt and van Duin is not explicable on this hypothesis.

The effect of non-electrolytes on the electrokinetic potential is well exemplified in the following curves obtained by Mukherjee (*J. Ind. Chem. Soc.* v. 703, 1928) for the influence of non-electrolytes on sols of arsenious sulphide.



If the non-electrolytes are in fact selectively adsorbed it necessarily follows that the ions are displaced from the colloid surface; thus the non-electrolyte cuts down the adsorption of the ions of the added electrolyte. It has already been noted that the anions and cations of an added salt are not equally adsorbed and it is likely that the extent to which the ionic adsorption is cut down by the preferential adsorption of the non-electrolyte is not equal for each ion. In the case of the negative arsenious sulphide sol if the non-electrolyte cuts down the adsorption of the cation of an added salt more than the anion a decrease in sensitiveness will result; if the anion adsorption is preferentially cut down an increase in sensitiveness will naturally obtain.

This hypothesis has been tested experimentally by Rideal (*Proc. Camb. Phil. Mag.* XXIV. 101, 1924) and by Weiser (*J.P.C.* XXXVIII. 1255, 1924); both the liminal concentrations required for precipitation and the actual adsorptions of the precipitating ions in the presence of various sensitising agents were determined. This explanation cannot however be generally applicable for tannin according to Brossa (*Koll. Zeit.* XXXII. 107, 1923) sensitises both positively and negatively charged dyes to electrolytes. Kruyt suggested (*Zeit. physikal. Chem.* C. 250, 1922; *Koll. Zeit.* XXXI. 338, 1922) that the polar portions of the tannin molecule were adsorbed by the dye, rendering the outside less polar and thus more sensitive to electrolytes.

A similar interpretation cannot be given to the results of Sen (*Koll. Zeit.* XXXVIII. 311, 1926) who noted that there was an increased adsorption by manganese dioxide sols for both copper sulphate and silver nitrate in the presence of various non-electrolytes such as methyl and ethyl alcohol and especially cane sugar, although the manganese dioxide sol was stabilised by the non-electrolytes against copper sulphate but sensitised to precipitation by silver nitrate.

14. Precipitation by protective colloids.

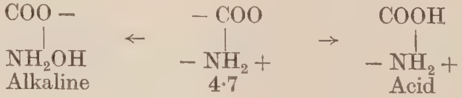
As has already been noted certain solvated colloids are readily adsorbed by colloidal suspensions such as gold or platinum and protect them, i.e. decrease their sensitiveness to precipitation by electrolytes. Experiments by Zsigmondy (*Gött. Nachrichten,* II.

177, 1916) and Gann (*Kolloidchem. Beihefte*, VIII. 252, 1916) have shown however that many of these "protective" colloids will precipitate gold suspensions when employed in small quantities. A comparison of the precipitating power of various protective colloids was made by the determination of the inversion number *U* which is the weight in milligrams necessary to convert 10 c.c. of an acid red gold sol into the violet form. As typical of the *U* numbers obtained the following may be cited.

Substance	Immersion number
Glycocol	> 80
Histidine	0·10–0·20
Peptone	0·04–0·06
Enepeptone	0·02–0·04
Albumose	0·002–0·004
Gelatine	0·002–0·004
Aniline hydrochloride	8–12
p-Amidophenol hydrochloride	2–3
1-2-4-diamidophenol hydrochloride	0·10–0·20
p-Amidodiphenylamine hydrochloride	0·04–0·06
Tetramethyldiamidobenzophenone	0·03–0·05
Malachite green	0·0025–0·004
Methyl violet	0·002–0·003
Fuchsine	0·002–0·004
Casein	0·002–0·004
Haemoglobin	0·005–0·003

According to Gann (*loc. cit.*) the precipitative power of such substances is dependent on the presence of an amino group and is thus constitutive.

In reality this assumption is not warranted as will be evident from the following considerations. We may regard amino acids consisting essentially of amphoteric ions in solution. At the isoelectric point the acid and basic dissociations of the amphoteric ion are equal whilst on the acid side of the isoelectric point we obtain positively charged cations, on the basic alkaline side negatively charged anions. Thus gelatine of isoelectric point $P_H = 4{\cdot}7$ on the acid side supplies (gelatine *H*) ions, on the alkaline side furnishes gelatinate ions



$$\begin{array}{ccccc} \mathrm{COO}- & & -\mathrm{COO} & & \mathrm{COOH} \\ | & \leftarrow & | & \rightarrow & | \\ \mathrm{NH_2OH} & & -\mathrm{NH_2}+ & & -\mathrm{NH_2}+ \\ \text{Alkaline} & & 4{\cdot}7 & & \text{Acid} \end{array}$$

A solution of gelatine brought into contact with a colloidal solution of negatively charged gold less acid than P_H 4·7 will exert a protective action due to the adsorption both of the amphoteric ions and of the negatively charged gelatinate ions, but if brought into contact with gold more acid than P_H 4·7 the positive gelatine ions will be adsorbed and lower the interfacial potential of the gold resulting in precipitation. Further addition of acid gelatine, however, results in dispersion and we shall obtain a stable but positively charged gold sol.

Thus any amphoteric electrolyte may cause similar variations in precipitative power on each side of its isoelectric point. In the following table are given the isoelectric points of a few typical amphoteric electrolytes.

Amphoteric electrolyte	Isoelectric point
p-Amino benzoic acid ...	$7{\cdot}2 \times 10^{-3}$
Aspartic acid	$1{\cdot}1 \times 10^{-3}$
Trypsin	3×10^{-4}
Casein	2×10^{-5}
Gelatine	2×10^{-5}
Arsenious acid	$2{\cdot}4 \times 10^{-5}$
Tyrosin	$3{\cdot}9 \times 10^{-6}$
Denatured serum albumen	4×10^{-6}
Serum globulin	4×10^{-6}
Oxy-haemoglobin ...	$1{\cdot}8 \times 10^{-7}$
Alanin	$6{\cdot}1 \times 10^{-7}$
Glycocol	$8{\cdot}2 \times 10^{-7}$
Leucin	$8{\cdot}8 \times 10^{-7}$
Lysin	3×10^{-10}
Arginine	3×10^{-11}

The isoelectric point of an amphoteric electrolyte is likewise displaced by the addition of neutral salts as is instanced by the following values for chromated gelatine in the presence of various neutral salts.

Electrolyte	Isoelectric point
Na_2SO_4	$10^{-3\cdot6}$
$Na_2C_2O_4$	10^{-4}
NaCl	$10^{-4\cdot3}$
KCl	$10^{-4\cdot3}$
$BaCl_2$	$10^{-4\cdot8}$
$Co(NH_3)_6Cl_3$ ...	$10^{-7\cdot0}$

Kennedy and Wright (*Biochem. J.* XVII. 635, 1923) have shown that gelatine at a P_H of 4·7 exerts but little protective power on a negative gum benzoin sol, acid gelatine precipitates the colloid in small concentrations whilst alkaline gelatine protects it. Similar observations have been made by Zsigmondy on the effect of casein on gold, but its exact isoelectric point was not established.

CHAPTER IX

GELS AND HYDRATED COLLOIDS

1. Introduction.

In many cases of precipitation from solution the precipitate does not come down in a granular form but forms a jelly which is a rigid mass containing appreciable quantities of solvent and possessing properties akin to a solid. There is no marked definite transition point which distinguishes a granular precipitate from such a jelly or gel, thus we have seen that barium sulphate usually distinctly granular and microcrystalline may, under suitable conditions, be precipitated in a form in which the aggregates enclose a certain amount of water. The hydroxides of iron and copper precipitated at low temperatures appear as flocculent masses of macroscopical size and possessing a certain loose structure, whilst precipitation at high temperature results in the formation of granular precipitates. More gelatinous in character are the precipitates of alumina, silica and gelatine. The flocculent precipitates are evidently particles of a true gel which possesses but little mechanical resistance and are readily broken up by mechanical or thermal agitation. Gels can only be formed by process of precipitation either as a result of the interaction of two reagents or by cooling a solution containing the gel-forming material which possesses a positive temperature concentration coefficient.

2. The structure of gels.

Several theories have been proposed to explain the process of gel formation, and diverse views are held as to their actual structure. The conditions favourable to gel formation are experimentally determinable and have to be considered in relationship to the theories proposed (Svedberg, *Herstellung kolloider Lösungen*, 1909; *Trans. Farad. Soc.* xvi. 3, 1921). The factors favourable to precipitation in the form of a gel are the following:

(1) High solvation of the particles.

(2) High number of particles per unit volume.

(3) Small difference in specific gravity between particles and liquid.

(4) No stirring of the system.

(5) Low temperatures which favour 1 and 4.

At one time it was considered that the gels were homogeneous or one-phase systems. Evidence in support of this hypothesis has been advanced by Pauli (*Kolloid Chem. d. Eiweisskörper*), Katz (*Koll. Zeit.* IX. 1, 1917), Procter (*J.C.S.* CV. 303, 1914) and Loeb (*J. Gen. Physiol.* III. 827, 1921; IV. 73, 97, 351, 1921–1922). The investigations of Procter and Loeb were confined chiefly to the chemical behaviour of gelatine (see p. 425) and to the phenomenon of swelling in this gel, a subject investigated systematically by Katz and extended by him to a variety of substances. Although an explanation of certain properties is afforded by the one-phase theory, there are many others, e.g. the actual mechanism of gelatinisation, the alteration of viscosity with the rate of shear, elastic fatigue, and others which are not so readily interpreted on this basis. The ultimate test of the theory, however, is to be found in the optical resolution of the two phases, if they exist, by means of the microscope or ultramicroscope. Such a resolution into two phases is for many substances undergoing gelation by no means easy (Zsigmondy, *Kolloidchemie*, ch. 62, 1920), e.g. for gelatine, starches, and the polypeptides, since not only may the refractive index of the substance differ but a slight extent from the environment, but owing to the high solvation of the particles visibility is still further diminished. Again since most gels possess a large number of particles per unit volume, light scattering in the Tyndall beam may be general over the field of vision and isolation thus rendered impossible.

Many gels, however, readily permit of optical resolution into two phases, and there is little doubt, owing to the general similarity between the various gels that all of them are in fact two-phase systems. The close similarity in properties such as diffusivity, refractive index and electrical conductivity of the sol and gel forms of substances like gelatine and the soaps (Graham, *Proc. Roy. Soc.* 1864; Arrhenius, *Öfvers. Stockh. Akad.* VI. 121, 1885; Walpole, *Koll. Zeit.* XIII. 241, 1913; McBain, *J.C.S.* CXVII.

1806, 1920; *Proc. Roy. Soc.* A, XCVIII. 395, 1921) again support the hypothesis that there is no abrupt change in physical state in the transition from the undoubtedly diphasic sol to the gel. The weight of experimental evidence is thus in general, although in some cases not conclusively, opposed to the one-phase theory of gelation, and a two-phase structure is generally assumed.

3. Two-phase theories of gel structure.

Various hypotheses have been advanced as to the nature of these separate phases which may conveniently be divided into two groups, those which favour an immiscible liquid-liquid system, and those which hold that gels consist of a solid-liquid system.

In the case of emulsions it was noted that there was no apparent limit to the ratio of the internal or disperse phase to the external or continuous phase. The disperse particles at first spherical under the action of surface tension could undergo close packing and assume a polyhedral or honeycomb structure. Under these conditions the external phase may be reduced to a mere skin forming the walls of the polyhedra. If this skin be a viscous liquid the emulsion will acquire a considerable mechanical strength and rigidity and may in effect possess solid properties forming an emulsion gel or grease. This two-phase theory of gels was first advanced by Bütschli (*Untersuchungen über Structuren*, 1898) from microscopic examination of a number of coarse gels in which signs of a cell wall were obtained, and was given support by the investigations of Van Bemmelen (*Die Adsorption*) on the vapour pressure of gels undergoing gradual desiccation confirming the existence of pores, presumably within a network. The two-phase liquid-liquid concept of gels was likewise advanced by W. Ostwald (*Pflüger's Archiv*, CIX. 277, 1905; CXI. 581, 1906) who assumed that a gelatine gel, for example, consisted of a solution of gelatine in water in a solution of water in gelatine, the two liquids possessing a definite interfacial surface tension. If the two liquids are perfectly homogeneous these gels would differ from the emulsion gels only in that the latter possess a third substance which goes to the interface diminishing the interfacial surface tension, whilst in the former no such extraneous stabilising agent is present. In a gelatine gel for example, on increasing the gelatine concentration in the water, the water in gelatine phase grows at the expense of the gelatine in water, and the spherical particles of the discontinuous phase will grow both in number and in size. If the similarity between the emulsion gels or greases and gelatine persists evidently the honeycomb structure will obtain as the final form of a rigid gel.

The honeycomb theory of gels rigidly assumes the existence not only of two phases but of a disperse and a continuous phase, the continuous phase forming a network. The gelatine gel however differs from a true emulsion gel in that there is no stabilising agent, i.e. since there is no film at the interface, two spheres of the water in gelatine phase in close proximity to one another should, instead of producing a mutual distortion and flattening of the spherical surface, actually coalesce, resulting in the formation of an interlacing system of two continuous phases, a view supported by Bancroft (p. 242) who points out that with a still further increase in the gelatine content of the gel water may actually be dispersed in definite drops in the gelatine phase.

4. The solid-liquid theory of gel structure.

Hardy (*Proc. Roy. Soc.* B, LXVI. 95, 1900) adopted a somewhat different hypothesis, suggesting that, in the case of gelatine, the gelatine phase was not, as supposed by Ostwald and Bancroft, a highly viscous liquid, but actually a solid solution. The gel would thus consist of a solid solution of water in gelatine containing within it a disperse phase of gelatine in water. Support to this hypothesis has been given by Freundlich (*Kapillarchemie*), by Fischer (*Soaps and Proteins*, 1921) and by Anderson (*Zeit. physikal. Chem.* LXXXVIII. 191, 1914). The outstanding difficulty in these assumptions is that a dilute solution of gelatine certainly consists of two phases of which one is assumed to be either a viscous or a solid solution of water in gelatine, and the other one of gelatine in water; the former is present in small quantities and the liquid is mobile. The solid phase must therefore be the discontinuous phase. Yet on gelatinisation it is assumed that the viscous or solid phase is continuous; this necessitates an inversion of the phases during gel formation, a point of view negatived by the close similarity between the sols and the gels in their permeability to diffusion and electrical conductivity. Furthermore this inversion would appear to be somewhat difficult of experimental realisation if the water in gelatine phase were actually a solid, as supposed by Hardy, but certainly possible with a viscous liquid.

These difficulties involved in the two-phase theory of gel formation on the assumptions of a continuous highly viscous or solid phase enclosing a liquid within its pores do not arise if the reverse be assumed to present a picture of gel formation, i.e. a continuous liquid phase enclosing the highly viscous or solid material as the discontinuous phase. In the case of the emulsion gels or greases the rigidity of the system is created by the mechanical strength of the continuous phase; such a rigidity is not necessarily excluded if the continuous phase be liquid, for example a cadmium gel in alcohol (Svedberg, *Trans. Farad. Soc.* XVI. 55, 1921), but is somewhat improbable. The characteristic elasticity of such gels is furthermore somewhat difficult to explain if the property be due to a series of isolated spherical elastic particles embedded in a relatively non-compressible and inelastic medium.

5. Gel fibrils.

These two characteristic qualities of the gels are best interpreted on the assumption that the disperse phase does not consist of isolated particles but that union between a number of these particles takes place to form relatively short fibrils or threads, which intersect one another to form a felt in the irregular meshes of which the mobile liquid phase penetrates. The fibrils in the case of gelatine would, according to Bancroft, consist of a viscous water in gelatine solution, and, according to Hardy, a solid solution of water in gelatine.

The fibrillar nature of gels was first tentatively suggested by Bütschli who thought that the threads noted under high magnification were sections of a cell wall. Similar fibrils have been noted for a great variety of gels, notably by Zsigmondy (*Phys. Zeit.* XIV. 1098, 1913; *Zeit. anorg. Chem.* LXXI. 356, 1911), Bachmann (*ibid.* LXXIII. 125, 1911; LXXIX. 202, 1912), Barratt (*Trans. Farad. Soc.* XLIX. 16, 1920), McBain and others.

The fibrils are produced as the result of the partial coalescence of a disperse medium consisting of a highly viscous liquid or a solid solution. According to the solid-liquid theory the fibrils are produced by the coalescence of the dispersed sol in the form of crystalline threads, i.e. the fibrils themselves are crystalline in their nature. Doubtless the fibril crystals are highly hydrated, and the fibril may thus be considered to contain both dispersion medium and disperse gel-forming material. Evidence is in fact available from the study of soap, gels and curds that the hydration of the fibrils may be varied affecting the properties of the system.

That the fibrils were definitely crystalline was suggested by Flade (*Zeit. anorg. Chem.* LXXXII. 173, 1913) as a result of examination of the gel of barium malonate in methyl alcohol, a point of view supported later by Stübel (*Pflüg. Archiv*, CLVI. 361, 1914) and Howell (*Amer. J. of Physiol.* XL. 526, 1916). The X-ray examination of a number of gels, including silica, stannic oxide and vegetable fibres, such as cellulose and ramie fibre, by Scherrer (*Nach. Ges. Wiss. Göttingen*, p. 96, 1918) has confirmed the presence of a crystalline structure in these gels. Gelatine on the other hand exhibited no crystalline interference lines, but was found to be amorphous.

The crystalline structure of the fibril is likewise supported by a study of the crystal habit of a number of substances which can, with care, be made to gel. Benzopurpurin and chrysophenone crystallise readily in rigid needle-like crystals. Gels can likewise be prepared from these substances in which long gelatinous needle-like crystals have been observed. Needle-like crystals can likewise be obtained from solutions of dibenzoyl cystine which undergoes gelation with great readiness (Gortner, *J.A.C.S.* XLIII. 2199, 1921). The crystals obtained from these substances are of varied character, occasionally short and relatively stiff, as is probably the case in nitrocellulose and in dibenzoyl cystine, and at other times long, thin and flexible, as in benzopurpurin and the product formed by the interaction of iodine and cholic acid. The thin, flexible crystals will readily pass through a filter paper, and, under the microscope, are in continuous agitation, performing a series of twisting and spiral movements as a result of

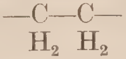
Brownian bombardment. It appears likely that the nature of the crystal thus formed is the governing influence in the rigidity and elasticity of the resulting gel.

The X-ray examination evidently provides a ready classification of the gels into the crystalline and non-crystalline varieties, of which the most well known is gelatine.

6. Rigid and moist gels.

But little is known as to the influences which affect the growth of crystals in the fibrillar form. There are evidently two methods of growth for a short fibrillar crystal, it can grow either longer or broader. In the regular growth of crystallisation the two growth rates are commensurate with one another; for the fibril an elongated and slender crystal is necessary, the more inelastic and drier the gel so much coarser is the fibril, i.e. its axial growth rate relative to its longitudinal is greater. It will be noted that, in those cases where the chemical constitutions of the gel-forming material have been determined, they are almost invariably long molecules, e.g. the higher fatty acids in the soaps, the amyloses in starch and amino acids in albumin. The long molecules have in addition frequently, as is the case also in liquid crystals, a reactive group at each end of the molecule and always at one end. It appears probable that the molecules permitting growth in échelon are those in which fibril formation and hence gelatinisation are possible.

In the case of dibenzoyl cystine the effect of substitution of various groups in the molecule on its properties of gelatinisation supports this hypothesis of growth in échelon.

The replacement of the unsaturated —S—S— linkage by a saturated linkage such as  $—\underset{H_2}{C}—\underset{H_2}{C}—$ destroys the power of gelatinisation; the replacement of the electro-negative benzoyl group by a more electro-positive group such as —H or —CH_3CO likewise destroys this property; substitution by the *p*-chlor or *p*-nitro benzoyl, however, does not destroy it. On replacement of the hydrogen of the carboxyl by a more electro-positive element, such as sodium, the property of gelatinisation is likewise lost.

A similar chain formation has been suggested by Pauli (*Trans.*

Farad. Soc. XIV. 10, 1921) for the composition of the sols and gels of the inorganic colloidal hydroxides, e.g. zirconia produced by the hydrolysis of zirconium oxychloride. By electro-potentiometric measurements of the hydrogen and chlorine ion concentrations of sols formed by hydrolysis, as well as freezing point, conductivity and transport number determinations, he has shown that a series of salts are formed of the types:

$$\left[\mathrm{Zr(OH)_4 . Zr(OH)_4ZrOCl_2Zr\,\overset{++}{O}}\right]\overset{--}{\mathrm{Cl_2}},$$

$$\left[\mathrm{Zr(OH)_4 . ZrOCl_2Zr\,\overset{++}{O}}\right]\overset{--}{\mathrm{Cl_2}},$$

$$\left[\mathrm{Zr(OH)_4 . Zr\,\overset{++}{O}}\right]\overset{--}{\mathrm{Cl_2}},$$

as well as the complex zirconic acid $\left[\mathrm{Zr(OH)_4ZrOCl_2\overset{--}{Cl_2}}\right]\overset{++}{\mathrm{H_2}}$, whilst in a similar manner he was able to identify the following in the gel-forming sols,

$$[x\,\mathrm{Fe(OH)_3}\,y\,\mathrm{Fe}^{\cdot\cdot}],$$

$$[\mathrm{Al(OH) . Cl_2 . Al(OH)_2Cl}],$$

$$[\mathrm{2Al(OH)_3Al(OH)_2Cl}] \text{ and } \left[x\,\mathrm{SnO}\,y\,\mathrm{Sn}\,\overset{--}{\mathrm{O_3}}\right]\overset{++}{\mathrm{K_2}}.$$

7. The imbition of liquids by gels.

The ultramicroscopic examination of a gelatinising sol reveals the presence of very small particles termed ultramicrons; it is assumed on the fibrillar theory that the ultramicrons aggregate to invisible threads or fibrils. As the gelatinisation proceeds the fibrils thicken and lengthen and in many cases may actually be rendered visible by powerful magnification under the microscope. The fibrils are diffused at random in the form of a felt through the material and may, as we have noted, be markedly crystalline in the filamentous, somewhat flexible in the fibrillary and distinctly mobile and flexible in the streptococcic forms visible under the microscope.

The characteristic properties of the gels are dependent on the nature of the fibrils, the more coarse the fibrils the more moist and elastic the gel, the finer the fibril the drier and more rigid the resultant gel; silica gel may be taken as representative of a dry rigid fine fibril gel and gelatine as that of the relatively coarse elastic type.

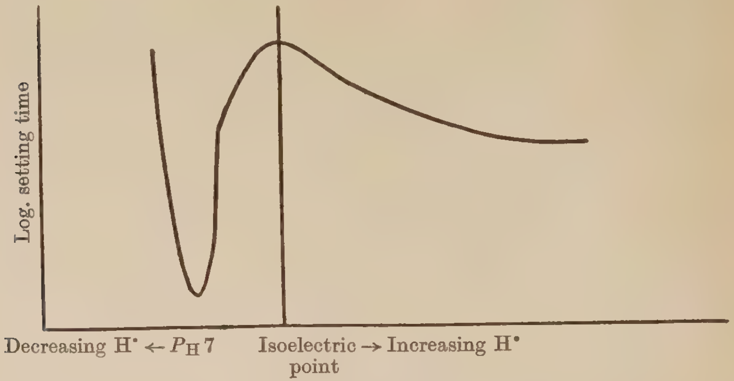
8. Rigid gels.

On drying a rigid gel the aqueous phase enmeshed in the felt-like fibrils begins to evaporate, the gel is sufficiently rigid as not to collapse as the interfibrillar spaces become emptied of water and filled with air. Such a gel will, on immersion in other solvents, e.g. toluene, benzene or alcohols, imbibe the liquid.

Coarse elastic gels, such as gelatine or rubber, on the other hand, on drying begin to contract; the fibrils collapse or flow together as the interfibrillar water is removed. On immersion of the dried gel in various solvents imbition does not take place through the mechanical process of filling up empty pores, but only occurs if the liquid is actually adsorbed by the fibrils and is capable of redistending the gel. Imbition for the elastic gels is actually a case of adherence to the fibrils and is only caused by liquids possessing this property, e.g. water in the case of gelatine and benzene and similar nonpolar solvents in the case of rubber.

9. The properties of silica gel.

Silica may be taken as a typical representative of a number of gel-forming hydroxides which may be either acidic or basic in their nature, e.g. tin, aluminium and iron, the acids of titanium, molybdenum and tungsten. Its preparation may readily be accomplished by the interaction of water glass (*ca.* 2 % SiO_2) and hydrochloric acid, although to obviate the subsequent removal of dialysable salts, hydrolysis of silicon tetrachloride or organo-silicon compounds has been suggested. The initial solution of ortho-silicic acid formed in this manner is unstable and is rapidly converted into the two-phase system; a sol of hydrated silica fibrils in a dilute solution of silicic acid (Mylius and Groschuff, *Ber.* XXXVIII. 116, 1905). The sol thus formed is not very stable but slowly increases in viscosity as the fibrils link up with one another until a rigid gel is obtained. The conversion of sol into gel is not reversible and is affected by a number of factors, thus the rate of sol-gel transformation is very considerably increased on elevation of the temperature (Fleming, *Zeit. physikal. Chem.* LXXXVI. 493, 1912) and also by the presence of various electrolytes. The sol particles of this relatively weak acid undergo surface ionisation yielding a negatively charged colloidal solution, and the sensitivity of the setting time to hydrogen and hydroxyl ions is evident from the following curve.



The unstable sol evidently possesses a maximum stability at the isoelectric point in contrast to the suspensions.

Very high concentrations of neutral salts are required to effect rapid gelatinisation of the silica sol (Hardy, *Zeit. physikal. Chem.* XXXIII. 391, 1900; XLIII. 11, 272, 1903; Pappada, *Gaz. Chim. Ital.* XXXV. 1, 78, 1905).

Thus Pappada obtained the following values for the time in hours necessary to effect complete gelatinisation on the addition of 1 c.c. of electrolyte to 2 c.c. of a silica sol containing 6 grm. SiO_2 per litre.

	$\frac{SO_4''}{2}$ (0·033M)	Cl′	NO_3'
Cs	36	37	57
Rb	82	72	90
K	106	122	116
Na	139	166	172
Li	188	216	280

The anion, as is to be expected in the case of a negatively charged colloid, evidently exerts but little effect. The sol-gel transition is generally examined by means of observation of the change in viscosity of the solution. The changes in viscosity as measured by the flow method in an Ostwald or similar apparatus differ as a rule somewhat widely from the values obtained by the shearing process employing a rotating cylinder or oscillating pendulum. The determination of viscosity involves a rupture of a certain number of the fibrils when a shear method is employed, whilst in the viscosometer the apparent viscosity will be widely different as the fibrils orientate themselves either in the stream line of the flow or at random directions. Such orientation of long and thin particles has been clearly observed in the case of the sol of vanadium pentoxide by Freundlich (*Physik. Zeit.* XVI. 413, 1913) and Kruyt (*Koll. Zeit.* XIX. 161, 1916). No satisfactory formula has as yet been proposed for the dependence of the viscosity of a sol on the molecular concentration of the sol-forming material. Amongst those that have been proposed are those of Arrhenius (*Zeit. physikal. Chem.* I. 255, 1887) and Kendall (*Med. k. Vetenskap. Nobelinst.* XXI. 251, 1913),

$$\log \frac{\eta}{\eta_\infty} = KC,$$

where η_∞ is the viscosity of the medium and C the molecular concentration.

That of Hatschek has been found to possess a somewhat limited application to solutions of pseudo globulin and albumin, the formula proposed is $\frac{\eta_\infty}{\eta} = 1 - \sqrt[3]{\phi}$, where 100ϕ is the volume percentage of dissolved substance and its associated solvent (*Koll. Chem.* VIII. 34, 1911; XI. 284, 1912; XII. 238, 1913).

The formulae of Einstein

$$\frac{\eta}{\eta_\infty} = 1 + 2{\cdot}5\phi,$$

and of Hess (*Koll. Zeit.* XXVII. 1, 1920)

$$\frac{\eta}{\eta_\infty} = \frac{1}{1 - \alpha\phi} = 1 + \alpha\phi + \alpha^2\phi^2 \ldots,$$

are evidently closely related to that of Arrhenius and Kendall.

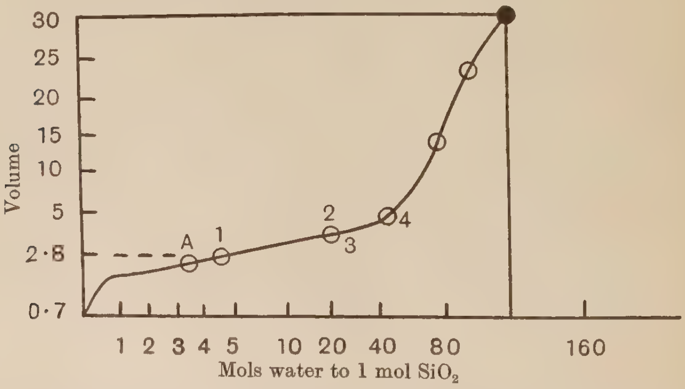
The behaviour of silica gel on desiccation and rewetting in water as well as in various organic liquids and gases has been investigated by Graham, Van Bemmelen $\{(CH_3\ COOH)\ (H_2O)\}$ (*Die Adsorption*, 1910), Bachmann (H_2O, CCl_3H, C_6H_6, $C_2H_2Br_4$,

C_2H_5I) (*Zeit. anorg. Chem.* LXXIX. 202, 1912), Anderson (C_6H_6, C_2H_5OH, H_2O) (*Zeit. physikal. Chem.* LXXXVIII. 191, 1914), Patrick (SO_2, NH_3) (*J.A.C.S.* XLII. 946, 1920; XLIV. 1, 1922) and Daniells (NO_2) (*J. Ind. Eng. Chem.* XV. 1173, 1923).

Gels containing over thirty mols of water to one of silica are relatively mobile, those containing twenty mols are stiff, with less water the gel becomes harder and can finally, with five or six mols, be ground up in a mortar to a fine powder.

On the progressive dehydration of a silica gel the gel rapidly contracts to a certain point, Van Bemmelen's "first inversion point," after which but little contraction takes place. On continued dehydration the clear gel suddenly becomes cloudy, then opaque, and finally loses its opacity again—Van Bemmelen's "second point" of inversion, when the water content has sunk to a ratio of one mol of water to one of silica.

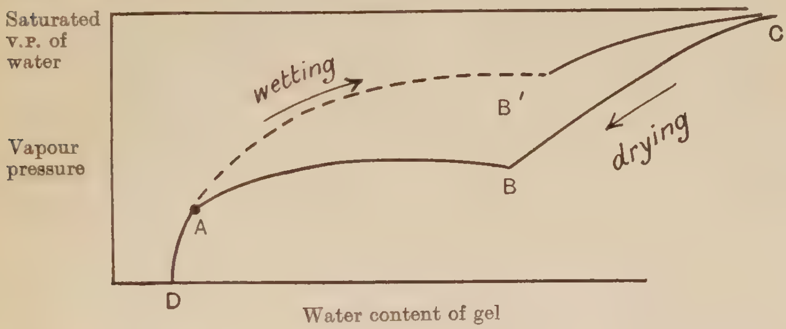
The volume change occurring on dehydration of a typical silica gel is shown in the following curve:



The change in vapour pressure on dehydration likewise indicates that the progress of dehydration is not uniform.

The curve can, in general, be divided into three parts, *CB*, *BA* and *AD*. Along the portion *CB* the vapour pressure gradually falls and the gel contracts; at *B* the contraction practically ceases, and the next portion of the curve *BA* is practically isopneumatic, evaporation taking place at constant pressure until *A* is reached where a rapid change in pressure occurs.

Provided that desiccation of the gel is stopped at the point D on rewetting the dried gel the vapour pressure rises along the curve DA, i.e. the process of hydration and dehydration in this range is perfectly reversible. As the water content increases the vapour pressure no longer follows the line AB, but the vapour pressures of the rewetted gel are somewhat higher than those obtaining during the process of desiccation, and follow the line AB'. At B' a similar break in the curve is obtained as noted during the period of desiccation and the vapour pressure rises rapidly along the line $B'C$. The vapour pressure curves cannot be interpreted on the assumption of the existence of definite hydrates which should present a uniformly stepped curve, but, as pointed out by Van Bemmelen (*Die Adsorption*) and Zsigmondy, actually support the fibrillar theory of gels. Along the region CB the free water is removed from the gel and the fibrils contract until further contraction without decomposition of the fibrils is impossible. Along the region BA the gel remains practically constant in volume whilst the interfibrillar water is removed. That the line BA is very nearly parallel to the x axis is an indication that the fibrillary mesh is relatively uniform. If the interfibrillar water be removed some contraction and coalescence of the fibrils one with another takes place, since the curve AB is not reversible, the higher vapour pressure on the rewetting indicating a smaller mesh. Nevertheless this contraction is but small, and the interfibrillar spaces left vacant by the water fill with air, and the gel in consequence becomes opaque due to internal scattering of light at the multitudinous water-air



interfaces until all the water is removed, when the gel becomes clear again. At *A* the interfibrillar spaces are completely emptied and the vapour pressure drops rapidly on further desiccation when the adsorbed water on the gel fibrils is removed. The removal of this water is a perfectly reversible process. After the adsorbed water is removed further dehydration of the gel results in disruption of the fibrils, which presumably consist of SiO_2H_2O, and the gel structure is definitely destroyed.

The hypothesis that the curve *AB* represents a nearly, but not quite, reversible process of filling and emptying the interfibrillary spaces is, as has been noted, suggested by the fact that but a small change in gel volume occurs and that the changes in transparency occur, as would be anticipated. Experimental data by Bachmann (*Zeit. anorg. Chem.* LXXIX. 202, 1912) and by Anderson (*Zeit. physikal. Chem.* LXXXVIII. 191, 1914) confirm this view.

Bachmann found that the volumes of various liquids imbibed by a silica gel within the region *AB* were approximately constant, although the molecular ratio of imbibed liquid to silica might vary over a very considerable range.

A few of Bachmann's data calculated on the assumption that no contraction in the various liquids occurs on imbition are tabulated below:

Liquid		Interfibrillary volume in c.c. per grm. gel
Gel 1.	Water	0·6210
	Benzene	0·6270
	Acetylene tetrabromide	0·6160
Gel 2.	Chloroform (1) ...	0·2902
	,, (2) ...	0·2923
	Ethyl iodide	0·2960

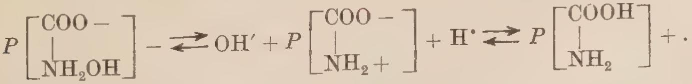
Attempts have been made to distinguish between "free" and "bound" water in gels from a determination of the fraction of the total amount of water present that is frozen (the "free" fraction) when the gel is cooled to the arbitrary temperature of

−20° C. The experiments of Thoenes (*Biochem. Zeit.* CLVII. 176, 1925) indicate that gels both of gelatine and agar can be frozen to this temperature repeatedly without much damage. With a 0·6 % gelatine at P_H 5·5 the amount of bound water was found to be 18·5 %; with a 13 % gelatine at P_H 5·3 the fraction was found to be 24·2 %. This distinction however between free and bound water cannot be maintained in the light of the work of Moran and Hardy (*Proc. Roy. Soc.* B, CXII. 47, 1926), where it was shown that save in very dilute gels a solid solution of gelatine and ice separates out on freezing.

A very interesting investigation has been carried out on silica gels by Rabinowitsch and Laskin (*Zeit. physikal. Chem.* CXXXIV. 287, 1928) on the neutralisation of silica in various states of dispersion by caustic soda. They conclude that the dissociation constant of colloidal silicic acid is $k = 2 . 10^{-4}$, a value to be compared with $k_1 = 10^{-9}$ (Hägg, *Zeit. anorg. Chem.* CLV. 21, 1926) for the acid in true solution. Since similar results were obtained with sols of arsenious sulphide they conclude that the surface dissociation of a solid acid exceeds the dissociation of the substance in true solution. The evidence presented cannot be regarded as conclusive and in the case of unimolecular films of the fatty acids the isoelectric point appears to be close to that anticipated for the acid in solution from data derived from a consideration of the homologous soluble acids. This point merits detailed investigation, as its bearing on the problem of the magnitude and nature of the electrokinetic potential is evident.

10. Gelatine and the Proteins.

The proteins consist essentially of amphoteric substances existing in equilibrium with both acidic and basic dissociation products of the type



$$P\begin{bmatrix}\mathrm{COO}-\\ |\\ \mathrm{NH_2OH}\end{bmatrix}^{-} \rightleftarrows \mathrm{OH}' + P\begin{bmatrix}\mathrm{COO}-\\ |\\ \mathrm{NH_2}+\end{bmatrix} + \mathrm{H}^{\cdot} \rightleftarrows P\begin{bmatrix}\mathrm{COOH}\\ |\\ \mathrm{NH_2}\end{bmatrix}^{+}.$$

Some like casein, salt-free globulin and acid albumin are not heavily solvated in solution and are thus readily precipitated at the isoelectric point in a manner similar to the suspensions already considered. Others, e.g. glutin, gelatine and natural albumin, are solvated like silica which at the isoelectric point are not necessarily precipitated, being maintained in the sol form by the solvent. On removal of the stabilising water however by the addition of alcohol or neutral salts, precipitation will occur, and this most readily at the isoelectric point. In an amphoteric substance the ratio of the electrically neutral particles to the total concentration is at a maximum at the isoelectric point, as is evident from the following considerations.

If c_A, c_K and x be the concentrations of the anionic, cationic and undissociated protein in a solution, then

$$c_A\, C_{\mathrm{H}} = k_a x,$$

$$c_K\, C_{\mathrm{OH}} = k_b x,$$

where k_a and k_b are the acid and basic dissociation constants of the amphoteric protein molecule. If the total concentration be n, then

$$x = n - c_A - c_K,$$

or

$$x = n - \frac{k_a x}{C_{\mathrm{H}^{\cdot}}} - \frac{k_b x}{C_{\mathrm{OH}'}},$$

or

$$\frac{n}{x} = 1 + \frac{k_a}{C_{\mathrm{H}^{\cdot}}} + \frac{k_b}{C_{\mathrm{OH}'}},$$

and

$$\frac{x}{n} = \rho \text{ the fraction of neutral particles}$$

$$= \frac{1}{1 + \dfrac{k_a}{C_{\mathrm{H}^{\cdot}}} + \dfrac{k_b}{C_{\mathrm{OH}'}}}.$$

In water as dispersion medium $C_{\mathrm{H}}\, C_{\mathrm{OH}} = k_w$ or

$$\rho = \frac{1}{1 + \dfrac{k_a}{C_{\mathrm{H}}} + \dfrac{k_b C_{\mathrm{H}}}{k_w}};$$

ρ is evidently a maximum when

$$\frac{1}{\rho} = \chi = 1 + \frac{k_a}{C_{\mathrm{H}^{\cdot}}} + \frac{k_b C_{\mathrm{H}^{\cdot}}}{k_w}$$

is a minimum or when

$$\frac{d\chi}{dC_{H^{\cdot}}} = -\frac{k_a}{C_{H^{\cdot}}^2} + \frac{k_b}{k_w} = 0,$$

hence
$$\frac{k_b}{k_w} = \frac{k_a}{C_{H^{\cdot}}^2},$$

or
$$\frac{k_a}{k_b} = \frac{C_{H^{\cdot}}}{C_{OH}},$$

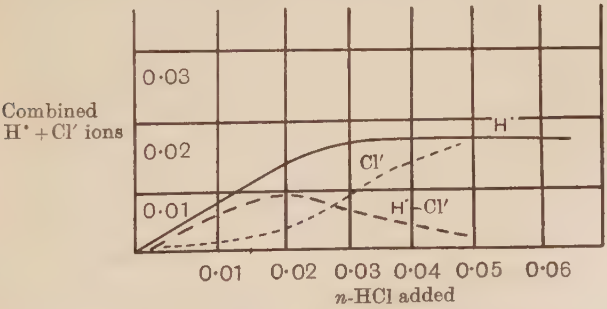
which is the isoelectric point.

On the progressive addition of an acid, e.g. hydrochloric acid, to an isoelectric protein, e.g. albumin, there will evidently be a progressive formation of the acid albumin AHCl. This will exist in equilibrium with its dissociated ions

$$AHCl \rightleftarrows AH^{\cdot} + Cl'.$$

The amount of undissociated albumin hydrochloride naturally increases with the addition of hydrochloric acid; thus if we plot the apparent fixation of both hydrogen and chlorine ions on the addition of hydrochloric acid to isoelectric albumin and also the difference between the hydrogen and chlorine ions adsorbed, we shall obtain a well-defined maximum for this difference at the point of maximum ionisation of the salt AHCl.

In the following curve are plotted the values obtained by Manabe and Matula (*Biochem. Zeit.* LII. 369, 1913) for ox serum albumin.

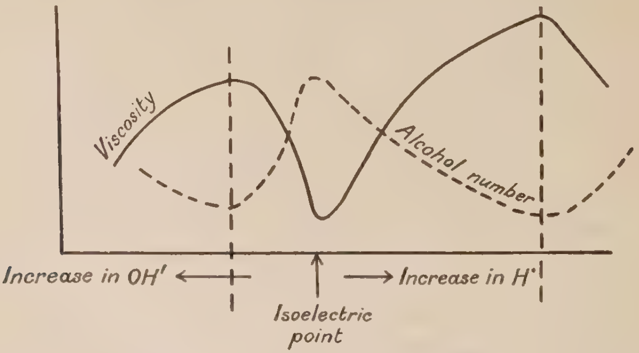


A similar point of maximum dissociation of the salt

$$NaA \rightleftarrows Na^{\cdot} + A'$$

will likewise be obtained on the addition of alkali to an isoelectric amphoteric protein.

Both isoelectric albumin and its undissociated acid and basic salts are less solvated and imbibe less liquid than the ionised form; thus the viscosity of an albumin solution will be least at the isoelectric point, rising to more or less well-defined maxima on each side, these maxima coinciding with the points of maximum dissociation of the two salts $\overset{+}{\mathrm{AH}} \vdots \mathrm{Cl}$ and $\mathrm{Na} \vdots \overset{-}{\mathrm{A}}$ into the heavily hydrated ions. Again the precipitation of such hydrated or lyophilic colloids involves essentially two distinct processes, the neutralisation of the electric charge by bringing the reaction of the medium to the isoelectric point and the desolvation of the electrically neutral particles. It appears that both isoelectric proteins and the undissociated salts, e.g. AHCl and NaA, are less heavily solvated than the ionic forms $\mathrm{AH}^{\cdot}$ and A'; thus the amount of alcohol required to precipitate a protein solution will evidently be least at the isoelectric point, greater on the progressive addition of alkali or acid, rising to more or less well-defined maxima at the points of maximum dissociation of the two salts and sinking with the increase of the undissociated salts. The variations in these properties are diagrammatically represented in the following curves:



Maximum dissociation of salt

$\mathrm{NaA} \rightleftarrows \mathrm{Na}^{\cdot} + \mathrm{A}'$

Maximum dissociation of salt

$\mathrm{AHCl} \rightleftarrows \mathrm{AH}^{\cdot} + \mathrm{Cl}'$

11. The structure of gelatine.

Bradford (*Trans. Farad. Soc.* XIV. 16, 1921) has attempted to prepare crystalline gelatine by utilising relatively dilute solutions of gelatine. According to Von Weimarn's hypothesis (see

p. 298) conditions favourable to the growth of crystals obtain in a solution of low viscosity and but a relatively small degree of supersaturation; by cooling a dilute solution of gelatine past the point of saturation extremely slowly it was hoped to obtain actual crystals. He obtained in a 0·4 % concentration globules or spherites of 0·1 μ diameter. The ultramicroscopic fibril of gelatine thus probably consists of a streptococcic chain of minute globules or spherites.

The structure of these spherites is uncertain; Bradford assumes that they consist of a regular crystalline growth formed by multiple twinning of minute crystals. Scherrer's examination of gold sols, however, has revealed the fact that the crystal interference lines are well developed when the particles contain as few as eighty molecules arranged in the cube lattice; a spherite of 0·1 μ diameter would probably show crystalline properties even if excessive twinning had taken place.

The investigations of Lehmann (*Flüssige Krystalle*), Vorländer (*Krystallinisch flüssige Substanzen*), Bose (*Phys. Zeit.* IX. 708, 1908; X. 32, 230, 1909) and Manjuin (*C.R.* CLII. 1680, 1911) on liquid crystals such as para-azoxy anisol, some of which, e.g. brom-phenanthrene sulphonic acid, are definitely colloidal, have shown that when these substances are immersed in a liquid in which they are insoluble there is a constant alternation between the liquid and the solid crystalline states at the melting point where the thermal agitation of the molecules just balances the cohesive power, the crystals frequently assuming the spherical form under the influence of surface tension. These swarms are definitely composed of minute crystals, since they exhibit the property of double refraction and are actually visible under a powerful magnification, but do not show the X-ray interference lines of true crystal structure (Van der Lingen, *Verh. d. Deutsch. Physik. Ges.* XV. 913, 1913), a phenomenon explicable on the hypothesis of the existence of orientated but unevenly spaced molecules. Kraemer (*J.P.C.* XXIX. 1523, 1925), from a study of the Brownian movement of mercury particles 200 $\mu\mu$ in diameter embedded in gelatine, concludes that the structure consists essentially of cubes of 5 $\mu\mu$ side stretched in chains 100 $\mu\mu$ from one another.

12. The properties of gelatine.

Commercial gelatine contains chiefly glutin and salts as impurities, the protein in the gelatine undergoes gradual hydrolysis to peptones and proteoses. Many of the physical characteristics of gelatine are dependent on the extent to which this hydrolysis has proceeded, e.g. its gelatinisation and muta-rotation (Bogue, *Chem. Met. Eng.* XXIII. 105, 1920; Smith, *J. Ind. and Eng. Chem.* XII. 878, 1920), and data obtained by various investigators on commercial and purified gelatine are consequently frequently at variance with one another.

The gel of gelatine differs from that of silica in that in the former the sol-gel transformation is reversible and not in the latter. The coalescence of the amicrons of gelatine to form streptococcic fibrils occurs at low temperatures, a process readily reversed by elevation of the temperature which decreases the amount of adsorbed water, increases the mobility of the fibrils, and permits of their rupture into smaller units. Gelatine is thus readily rendered more disperse by water.

Gelatine is an amphoteric electrolyte (Procter, *J.C.S.* CV. 313, 1914; Loeb, *J. Gen. Physiol.* I. 39, 237, 363, 483, 551, 1918–1919) having an isoelectric point at $P_{\text{H}} = 4{\cdot}7$. On the alkaline side salts or gelatinates, e.g. calcium gelatinate, are formed, whilst on the acid side we obtain soluble gelatine salts, e.g. gelatine chloride, whilst isoelectric gelatine is apparently almost insoluble in water.

Attempts have not been lacking to investigate how far the combination of acids and proteins such as gelatine may be regarded as an adsorption process and not as a true chemical reaction. If we assume that the combination of hydrogen ions for gelatine follows the Langmuir isotherm we obtain for the bound ions the expression

$$x = \frac{k_1 C_{\text{H}^\cdot}}{1 + k_2 C_{\text{H}^\cdot}}.$$

Rinde (*Phil. Mag.* I. 47, 1926) has performed this calculation with the experimental data given by Loeb and finds that the equation satisfactorily represents the experimental results with values of $k_1 = 14{\cdot}6$, $k_2 = 2100$.

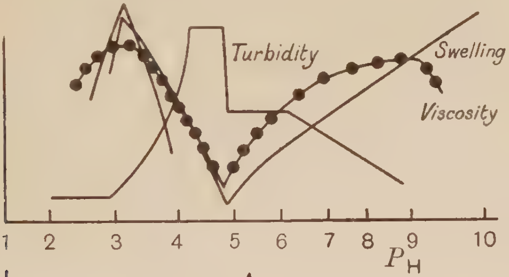
That the apparent agreement with the Langmuir isotherm can be taken as proof of the validity of an adsorptive mechanism is somewhat debatable, for we may observe that the simple law of mass action applied to a weak base and strong acid gives us

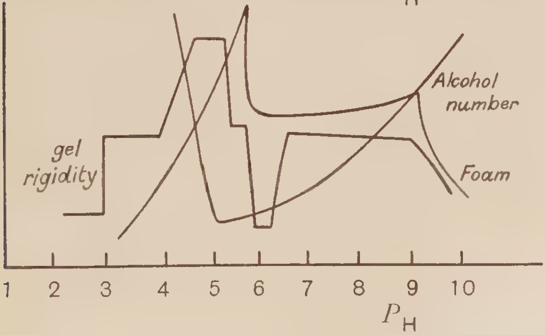
$$G + \mathrm{H}^{\cdot} \rightleftarrows G\mathrm{H}^{\cdot},$$

$$(1 - x)\,(C_{\mathrm{H}^{\cdot}}) = kx,$$

whence $x = \dfrac{C_{\mathrm{H}^{\cdot}}}{k + C_{\mathrm{H}^{\cdot}}}$, a form substantially that of the isotherm.

The influence of the hydrogen ion concentration on the various properties of the sol and gel forms of gelatine is most marked and has been investigated in detail by Loeb (*loc. cit.*) and Bogue (*J.A.C.S.* XLIV. 1349, 1922). A summary of the results of these investigations is given in the following curves representing the variation of the turbidity, viscosity, swelling, gel strength, foam and alcohol number with the P_{H}.





It will be noticed that all the properties of the gel with the exception of the turbidity and foam have minimum values at or near the isoelectric point $P_{\mathrm{H}} = 4{\cdot}7$, whilst these two attain their maximum values at this point. Evidently, as the data for the swelling and viscosity indicate, the hydration of the gelatine particles is at a minimum at the isoelectric point (see Chiari, *Biochem. Zeit.* XXXIII. 167, 1911) where, as indicated by the alcohol number, it is most readily precipitated from solutions to form large aggregates to which the turbidity and the foam formation are due.

13. The swelling of gelatine.

The imbition of a dried gelatine by the addition of water is accompanied by a heat evolution and the exertion of a swelling pressure. Rodewald (*Zeit. physikal. Chem.* XXIV. 206, 1897) obtained the following values for the heat of wetting:

% H_2O	Calories per grm.
0·23	28·11
3·23	20·97
8·16	12·43
12·97	7·37
19·52	2·91

whilst the variation in the swelling pressure with the gelatine content was found to obey an expression of the type

$$P = ac^k,$$

where a and k are constants. The volume of the original gel together with that of the added water is always greater than that of the final gel. A not inconsiderable contraction occurs which is accompanied by the heat evolution mentioned above. It will be noted that as the water content rises the swelling pressure and the heat evolution decrease and at the same time the consistency of the gel becomes less. A large portion of the water is readily removed by application of pressure, whilst dilute gels will on standing undergo contraction accompanied by a coarsening of the fibrils and an exudation of the contained and adsorbed liquid, a phenomenon frequently termed syneresis.

As in the case of silica gel the water in a gelatine gel may be removed and replaced by other liquids such as alcohol, benzene or chloroform (Bütschli, *Über den Bau quellbarer Körper*, Göttingen, XXII. 1896; Bachmann, *Zeit. anorg. Chem.* C. 1, 1907). Gelatine, however, is relatively much more elastic than silica, with the consequence that hysteresis is much more marked, and the portion of the vapour pressure curve indicating the emptying of the interfibrillary spaces which should be parallel to the x axis (see p. 423) is extremely small, denoting a progressive contraction of the mesh on removal of the containing fluid. Zsigmondy (*Kolloidchemie*, p. 373) has calculated the radius of the interfibrillary capillary as 70 Å., some three times larger than that for a similar silica gel.

The swelling of gelatine is, as has been noted, a minimum at the isoelectric point and increases on the addition of either acids or bases as well as on the addition of certain salts; thus with sodium salts the lyotropic series of decreasing swelling power is

$$CNS' > I' > Br' > NO_3' > ClO_3' > Cl' > H_2O > \text{acetate} > \text{citrate} > \text{tartrate} > SO_4''.$$

The swelling of such a gelatine is according to Procter (*J.C.S.* CV. 313, 1914; CIX. 307, 1916; *J. Amer. Leather Chem. Ass.* XI. 399, 1916) fully accounted for on the hypothesis that the conditions of equilibrium established between the gelatine in the interior of the thick fibrils and the interfibrillar liquid resemble those investigated by Donnan in his study on the behaviour of membranes separating a non-permeable ion from a solution containing membrane permeable ions.

We must assume that on the immersion of gelatine in a solution of a dilute acid, e.g. HCl, more acid than the isoelectric point $P_H = 4{\cdot}7$, the acid diffuses into the interior of the fibrils, resulting in the establishment of the following equilibrium:

$$HCl \rightleftarrows \text{gelatine } HCl \rightleftarrows \text{isoelectric gelatine}$$

Fibril	Interfibrillar liquid
$\overset{+}{GH}\ a$	$H^{\cdot}\ x$
$\overset{+}{H}\ b$	$Cl'\ x$
$Cl'\ c$	

As we have already noted (p. 353), the product of the diffusible ion concentrations in the interior of the fibril (b) (c) and in the interfibrillar liquid x^2 will be equal. Now for all values of b and c, $bc > x^2$ unless $b = c$, there will thus be an excess of diffusible ions in the interior of the fibril over those in the interfibrillar liquid. This excess of diffusible ions in the interior will produce an osmotic pressure proportional to the difference in concentrations and cause the fibril to swell.

On swelling, an increase in surface energy of the fibril will result and equilibrium will obtain when this increase in surface energy just balances the work done by the osmotic pressure in distension. It is of course possible to distend the fibrils beyond their elastic limits and thus cause disintegration of the gel.

The influence of neutral salts as well as of acids and bases on the swelling of gelatine, which we have seen can be attributed to an apparent change in the solvation of the gel fibrils and may be interpreted in the light of Donnan's theory of the effect of a non-diffusible ion on the osmotic pressure differences between the two phases, is likewise to be noted in the alteration of the viscosity and alcohol precipitation values of protein solutions. From the considerations already advanced there should exist two well-defined maxima in the viscosity and alcohol precipitation curves when these properties are plotted as functions of the P_H, the maxima coinciding with the points of maximum dissociation of the salts

$$\mathrm{AHX} \rightleftarrows \mathrm{AH}^{\cdot} + \mathrm{X}' \quad \text{and} \quad \mathrm{HA} \rightleftarrows \mathrm{H}^{\cdot} + \mathrm{A}'.$$

The studies of Pauli (*loc. cit.*) and his co-workers, however, have revealed the fact that isohydric solutions of different acids do not effect equal combination with the isoelectric protein; relatively more acetic acid, for example, being combined than hydrochloric acid in isohydric solutions. Again, both the actual position of these maxima as well as the magnitudes of the viscosities observed vary much with the nature of the acid employed. Thus the relatively weak oxalic acid appears to be a much stronger acid than sulphuric acid, whilst trichloracetic acid does not differ appreciably from acetic acid in its effect on the viscosity of albumin. It is probable that the degree of solvation of the protein molecules and of the protein salts must not be regarded as constant, but that they vary both with the nature of the salt and in the presence of neutral salts which exert like alcohol a desolvating action more or less complete on the solvated isoelectric protein as well as on the undissociated protein salts.

In the case of gelatine, as far as this substance has been examined with care, the simple molecule can be regarded as a monacid base and a monobasic acid possessing but one potentially reactive —CO OH group and but one reactive $—NH_2$ group in its molecule. The other proteins appear to be relatively more complicated; thus on the progressive addition of strong acids to proteins such as serum albumin a larger quantity of acid is taken up than on the addition of weak acids. Similar results are obtained with alkalis; the acid reacting power can further be enhanced by heat treatment with dilute acids (Adolf and Speigel, *Biochem. Zeit.* CIV. 175, 1920). These results are repeated in the case of alkalis; thus Pauli noted that the caseinate ion obtained on treating isoelectric casein with dilute soda was trivalent, possessing a mobility of $v_{\text{cas.}} = 30{\cdot}1$, but on adding excess of alkali the combining capacity of casein increases to a maximum apparent valency of thirty. There is naturally associated with this increase in valency an increase in the ionic mobility. Pauli indeed (*loc. cit.* CIX.) advances arguments for the assumption of the following stages in the ionisation of casein on the progressive addition of alkali:

$$\text{Isoelectric casein} \longrightarrow Na_3\,[(C''')\,C_x] \longrightarrow Na_3\,(C''') \longrightarrow Na_x\,C_x.$$

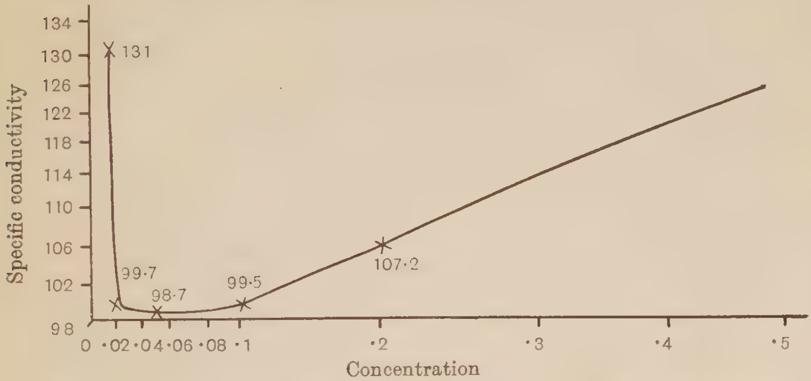
Whether the complex salt [Na_3C''' casein] must be regarded as a complex salt or an ionic micelle of the type investigated by McBain in his investigations on the soap solutions is not yet clearly established, whilst information on the acid and basic dissociation constants of the higher stages of dissociation of the complex protein is still lacking.

The globulins consist of simple proteins which are coagulated by heat treatment; they are not soluble or dispersed to a colloidal solution by water, but dispersion can be effected by dilute solutions of salts. On addition of excess of salt, e.g. ammonium sulphate, they are precipitated. Gortner and his co-workers (*Coll. Symp.* v. 179) have shown that the extent of peptisation as measured by the amount of extractable protein from a substance like flour is dependent on the nature of the salt employed, the salts giving a greater percentage of peptonic protein are found to be KI > KBr > KCl > KF, a lyotropic series which we have noted obtains in many other phenomena produced by salts. An important and interesting result was obtained when examining the proteins extracted in this manner. It was found that if the proteins extracted by means of potassium bromide were subjected to ionic purification by dialysis, the precipitated globulin would be redispersed by potassium chloride, although the quantity of protein originally extracted by the bromide was much greater than could have been extracted with potassium chloride.

14. The Soaps.

The soaps consist of the sodium and potassium salts of the higher fatty acids possessing marked detergent powers. In alcohol they dissolve to form optically clear solutions in which the salts possess the normal molecular weights. In water, however, although the salts of the lower fatty acids which possess no detergent powers behave in a normal manner, yet as the length of hydrocarbon chain increases these solutions become increasingly abnormal both in their properties and behaviour. Sodium capronate ($C_5H_{11}COONa$) is the first salt to show any anomalous behaviour in that the elevation of the boiling point of aqueous solutions of the salt does not proceed indefinitely with increasing concentration but rises to a maximum, and such strong solutions set to a gel on cooling. These abnormalities increase with the length of the hydrocarbon chain, the higher fatty acid salts showing but little elevation of the boiling point. Sodium laurate, however, is the first salt of the homologous series which may be said to possess all the properties of a true soap. The examination of the molecular and ionic state of aqueous soap solutions by physico-chemical methods is a matter of some difficulty owing to the abnormally small values observed in such determinations as the molecular elevation of the boiling point (Krafft and Stern, *Ber.* XXVII. 1747, 1894) or the lowering of the vapour pressure (A. Smits, *Zeit. physikal. Chem.* XXXII. 1584, 1899; XXXIX. 385, 1902; XLV. 608, 1903), whilst the osmotic pressure methods are vitiated by the effects produced due to the appearance of a membrane equilibrium (Moore and Roaf, *Kolloid. Zeit.* XIII. 133, 1913). The most successful method of determining the molecular state with the aid of the direct determination of one of these colligative properties of solutions is by the lowering of the dew-point, a method developed by McBain and Salmon (*Proc. Roy. Soc.* A, XCVII. 1920), by which the existence of molecular aggregates in aqueous solutions of the soaps was definitely established.

The examination of the electrolytic conductivity of soap solutions has, however, indicated that they are relatively good conductors and the conductivity concentration curve exhibits the interesting property of a definite minimum. The values for the specific conductivity of potassium palmitate are (McBain and Martin, *J.C.S.* CV. 957, 1914) plotted in the following curve:



The conductivity of the solution is not due to pronounced hydrolysis of the salt, since determination of the hydroxylion concentration of the solutions have been made by McBain and Martin (*loc. cit.*) and McBain and Bolam (*J.C.S.* CXIII. 825, 1918), both by means of the hydrogen electrode and by the rate of catalysis of nitroso-triacetonamine, the extent of hydrolysis is, as observable from the data on p. 438, relatively small.

The product of hydrolysis is naturally an acid soap of varying composition. In any dilute solutions of sodium palmitate it approaches that of the sodium hydrogen soap $NaHP_2$. McBain and Taylor found that the acid soap at 90° C. had the composition HP . 2NaP.

Potassium Palmitate

Soap conc. N	OH′ conc.	% hydrolysis
0·01	·0007	6·8
0·02	·0011	5·6
0·05	·0010	2·02
0·1	·0013	1·25
0·5	·0032	0·65
0·75	·0024	0·31
1·0	·0008	0·08

In order to account for the relatively high conductivity but low osmotic pressures and the low hydroxylion concentration of soap solutions, Bancroft assumed that the hydroxylions were adsorbed by the neutral colloidal potassium palmitate. This assumption was, however, proved to be incorrect by McBain, who showed that on the addition of caustic soda no adsorption of the added hydroxylions took place. As an alternative explanation McBain suggested that the conductivity was due to the part of the soap which existed in the colloidal state, a colloidal ion. The colloidal soap ion differs from the ordinary charged colloidal particle in that not only is its mobility great but the equivalent conductivity is high, the conductance, in fact, being much greater than that of the simple ion of the fatty acid from which it is derived and comparable to that of a potassium ion. To account for the high mobility and equivalent conductivity of the colloidal ion in an electric field, one must postulate that it possesses a relatively large charge for the number of molecules forming the aggregate and one must consider that the colloidal ion or ionic micelle (Nageli, *Pflanzenphysiologischen Untersuchen. Zürich*, 1858) is an aggregate of the ions of the fatty acid, the mobility of which will naturally be greater than that of the single ion since the resistance to motion of such an aggregate increases more slowly than does the charge. Such charged aggregate will, however, possess the small diffusibility of an ordinary colloid. There is a small but unmistakable difference between a potassium and a sodium palmitate solution, which has led McBain to the assumption that the ionic micelle contains in addition to the ions some undissociated soap molecules together with water of solvation, the diminishing value of which, as the concentration increases, accounts for the increase in the micelle mobility. Thus we ascribe to the ionic micelle of sodium palmitate the following composition:

$$(\mathrm{NaP})_a\,(\mathrm{P}')_b\,(\mathrm{H_2O})_c.$$

The value of b, the number of palmitate ions in the micelle, is at least ten. The examination of a solution of potassium oleate at a temperature of 0·18° C. by these methods has resulted in the following values for the concentrations of the various substances present.

Molality	Neutral colloid	Neutral salt	Ionic micelle	Oleate anion	Alkali ion
0·1	0·05–0·08	0·00–0·02	0·00–0·02	0·00–0·02	0·02
0·2	0·14–0·15	0·00–0·02	0·04–0·05	0·00–0·01	0·05
0·4	0·28–0·29	0·0	0·11	0·0	0·11
0·5	0·35–0·36	0·006	0·14	0·0	0·14
0·6	0·41–0·43	0·00–0·01	0·16–0·17	0·00–0·01	0·17

Aqueous soap solutions can be obtained in three distinct forms: the sol form containing the ionic micelle, a clear gel, and a white opaque solid, i.e. the curd. The sol and gel forms of various soaps have been examined by McBain and his co-workers and shown to differ only in elasticity and rigidity, whilst the electrical conductivity, refractive index, concentration of metallic ion and lowering of the vapour pressure are all identical, results to be anticipated on the fibrillar theory. The gel as we have seen is fibrillar in nature, and the conversion of a gel into a curd is brought about by the removal of soap from solutions in the form of relatively coarse fibres, a process similar to crystallisation. The experiments of Laing and McBain (*J.C.S.* CXVII. 1520, 1920) have shown, however, that a curd cannot be represented as a coarse gel felt of definite crystalline composition in equilibrium with a liquid phase, since the conductivity of a concentrated curd is higher than that of a dilute one, and the solubility diminishes with the age of the curd. In the case of gelatine gels the evidence for a hydration of the fibril material is definite; in the proteins a variation in the degree of hydration of non-ionised and ionised protein molecules had to be assumed, whilst in soap gels the fibrils are undoubtedly solvated. The variation in the conductivity of curds may therefore reasonably be attributed to a difference in the degree of solvation of the fibrils, the more heavily solvated fibrils according to Laing and McBain's experiments being more insoluble and thus more stable. The less solvated fibrils can only become converted into the more stable solvated form by a process of solution and recrystallisation, a somewhat lengthy process extending over several months in solutions of such low diffusivity as soap.

The abnormality of the sodium soaps of the fatty acids of high molecular weight to form complexes in solution consisting of neutral colloid soap particles and of ionic micelle is to be attributed to the action of the long hydrocarbon chains, which are in themselves insoluble in water and tend to adhere to one another as the experiments of Langmuir (see p. 90) have indicated. The detergent action and emulsifying power of soaps is likewise due to this cause. If we insert in an organic material, containing hydrocarbon chains sufficiently long so as to render their mutual lateral adherence great enough to overcome in part the disintegration due to the thermal agitation, polar groups of the type $—COOX$, $—CSSX$, $—SO_3X$, $—N(CH_3)_3I$, which are sufficiently strong to immerse the hydrocarbon chains, in water, we obtain substances possessing colloidal nature; detergent action, emulsifying powers, gel and curd-forming properties will naturally be obtained (Reychler, *Koll. Zeit.* XII. 277; XIII. 252, 1913). Such solutions, if the non-polar portion of the molecule be too short, or if too many polar groups be inserted, or again if the polar medium water be replaced by one somewhat less polar such as alcohol, will no longer possess colloidal properties but will behave as true solutions.

On separation of such substances from solution it is possible for the separated phase to be perfectly crystalline, as is the case with stearates and palmitates, or the substance can separate as a liquid crystal or in the smectic state; since this phase, when it exists at all, lies in between the unorientated liquid and the regular crystalline state, it has been termed the mesophase by Zocher (*Zeit. physikal. Chem.* CXLII. 113, 124, 177, 186, 413, 1929), who has examined the physical properties of materials in this phase state in some detail. We may regard such phases as the three-dimensional extension of a film existing in the liquid condensed or in the expanded state, provided that in the latter case the thermal agitation is not sufficient to complete the disorientation in layers superimposed on the basal film held to the liquid or solid substrate.

Zocher and Birstein (*ibid.*) have in fact observed a case in which the constitution of the mesophase can be altered by modification of the orientation of the basal film. *p*-azoxyanisol on alkaline surfaces forms a film in which the molecules are horizontal; on acid surfaces the molecules acquire a vertical orientation (see Ch. III); the mesophases formed on alkaline or acid surfaces take up the configurations of the basal film.

15. The colloidal dyes.

Solutions of various dyes on their dispersion in water vary from the highly dispersed state, in which the molecular weight determined by the usual methods is found to be perfectly normal, to relatively coarse suspensions. The degree of dispersity of a dye-stuff is partly constitutive in that the presence of polar or lyophilic groups increases the dispersity. The dye-stuffs are in this respect comparable to the salts of the fatty acids where the relative magnitudes of the non-polar or lyophobic and polar or lyophilic portions of the molecule determine the state of aggregation in dispersion in water. They differ, however, from the soaps in that the solvation both of the molecules and of the neutral colloid and ionic micelle of the colloidal dyes is not so pronounced. In consequence the dyes are more susceptible to electrolytes which, as in the case of the sols, readily produce flocculation or a change in the aggregation of the particles.

Many such changes in aggregation are associated with a variation in colour comparable to the colour change observed with gold sols; thus the red tint of colloidal congo rubin (Ostwald, *Koll. Zeit.* XXIV. 61, 1919) becomes definitely purple on the addition of acids, bases or salts to the suspension, whilst the addition of electrolytes to true solutions of fuchsin render it colloidal. An alteration in the polarity of the polar group appears likewise to affect the dispersion. Thus phenolphthalein undergoes practically complete dispersion in alkaline solution, i.e. when present as its sodium salt, but is colloidal when present as the free acid. In the soaps we note also a change in solubility affected by similar means from the insoluble fatty acid to the relatively soluble sodium salt.

The organic cations and anions are more strongly adsorbed than even the polyvalent inorganic ions; thus precipitation of colloids or apparently complete adsorption by a charged surface (of opposite electric sign to that of the dye ion or ionic micelle) will occur down to very low concentrations of the dye. In addition, as has already been observed, the somewhat lyophobic or sol-like character of the dyes, which renders them sensitive to electrolytes, will permit of wide variations in the size of aggregate effecting precipitation or undergoing adsorption. Associated with this variation in size is a definite change in colour affecting the colour of the dyed material. Non-colloidal dyes such as methylene blue, a positive ion, and eosine, an anion, may be utilised to precipitate colloids of opposite sign and will be markedly adsorbed both by charged suspensions and emulsions. Thus eosine is strongly adsorbed by silver halides stabilised with a positive charge, e.g. by excess of silver ions, but not by negatively charged halides, and can thus be utilised as an indicator.

Mutual precipitation of oppositely charged dye-stuffs is the basis of a number of volumetric processes of estimation; thus the evaluation of tannin solutions may be accomplished with night blue or of eosine with night blue.

The mechanism of dyeing (see *First Report on Colloid Chemistry, B. Ass.* 1917, for the complete résumé of the various theories) has received a great deal of attention and has led to the formulation of a variety of hypotheses such as the solid solution, the chemical, the adsorption and electrical hypothesis. A critical examination of the data on which these various alternative hypotheses rest would lead one to suppose that they are by no means irreconcilable with one another.

The process of dyeing appears to be an adsorption phenomenon; thus over a limited range in concentration the Nernst distribution law or the Freundlich isotherm will be obeyed, an observation confirmed by Georgievics (*Mitt. des K. K. Gewebe Museums in Wien*, pp. 165, 205, 349, 1904). Such adsorption compounds, however, are not similar to solid solutions as postulated by O. Witt, but due to true adsorption. As has already been noted, the chief factor in promoting adsorption is the decrease in the free energy of the system, i.e. a lowering of the interfacial energy in accordance with the Gibbs' law; although solid skins of fuchsin, peptones and saponin may be formed at air-liquid and liquid-liquid interfaces, it is improbable that any dyeing can result from such processes alone, as the fastness or the formation of solid films is due to subsequent chemical changes occurring in the Gibbs' layer. The dye-stuffs, whether in true or colloidal solutions, are all charged and are adsorbed by the material with the simultaneous neutralisation of their charge.

Cotton fibres are gel-like, usually negatively charged in water and readily adsorb basic colours; on increasing the negative surface charge of cotton by the formation of oxy- or nitro-cellulose, the affinity of the fibre for the basic colour is increased; the fibres of wool and silk are, like the proteins, amphoteric in their nature and can combine with both acid and basic dyes. Since the charge on gel fibrils is, as we have seen, localised at certain points along the fibril where the polar portions of the molecule are present, the adsorption of a dye-stuff at the point of saturation will be apparently stoichiometric, each polar group adsorbing its quota of dye. Thus in the adsorption of dye-stuffs in true solution an apparent chemical action takes place as maintained by Knecht (*J. Soc. Dyers and Cols.* 242, 1904). If, however, the dye be colloidal, the polar groups will still adsorb an electrical equivalent which will, however, be associated with a variable number of dye molecules dependent on the dispersity of the dye solution.

As has already been noted in other cases, the distinction between adsorption compounds and chemical compounds is chiefly one of stability of union. In the process of dyeing evidently the adsorption formed by the specific adsorption of polar groups in the fibre for ions or ionic micelle of the dye-stuff results in the formation of an adsorption compound which, however, will be relatively unstable and dyeing will not be fast. A closer union, however, results in the neutralisation of the electric charge on the dye ion and on the fibre and a process akin to coagulation takes place. The dye can now only be removed from the fibre by a strong peptising agent. Some apparently fast dyes may readily be peptised and removed from the fibre by replacing the water by an organic solvent which peptises the dye by adherence to the non-polar portion of its molecules.

16. Thixotropic gels.

We have already referred to the polyhedral structure of the solid greases and the fibrous or filamentous structure of true gels. In addition to these solid forms there exist a number of cases of colloidal solutions which can assume conditions of rigidity, but on gentle agitation will break down to a sol again. These forms have been termed by Freundlich thixotropic gels.

The phenomenon of thixotropy was first observed in concentrated sols of ferric oxide (Szegvari and Schalek, *Koll. Zeit.* XXXII. 318, 1923; XXXIII. 326, 1923; Freundlich and Rosenthal, *ibid.* XXXVII. 129, 1925; *Zeit. physikal. Chem.* CXXII. 403, 1926). Freshly prepared sols of ferric hydroxide from the chloride-like aluminium hydroxide, zirconia and thoria are completely amorphous under X-ray examination. On ageing, a diagram of crystalline basic monochloride and finally of goethite FeO(OH) is obtained. These crystals may be orientated in a magnetic field or by gentle streaming, and exhibit double refraction and dichroism under these conditions. They are thus probably lamellar-like rhombic particles; at rest these lamellae form very regular layers which may acquire a definite rigidity.

A similar thixotropic gelation has been observed in sols of the oxides of selenium, zirconium and tin, and is according to Freundlich and Bircumshaw (*Koll. Zeit.* XL. 20, 1928) especially marked in the case of alumina prepared by the hydrolysis of aluminium acetate. The time necessary for thixotropic gelation is greatly affected by the presence of salts as is instanced by the data on p. 445 for a 12·16 grm. per litre alumina sol.

There appears little doubt that these thixotropic gels are due to a species of structural coagulation in which the small true gel particles are arranged in a loose network which is readily broken up by mechanical agitation. The orientation of colloidal particles to rod-like forms is clearly observable in polarised light as shown by Zocher in sols of vanadium pentoxide, chrysophenin and benzopurpurin, whilst Usher (*Proc. Roy. Soc.* A, cxxv. 143, 1929) has followed the thixotropic gelation of sols of gamboge and cadmium sulphide on the addition of sodium chloride. The small aggregates resulting from partial coagulation were observed to form an expanding network which linked up with one another under the influence of Brownian agitation to form an open structure of linear aggregates.

Added NaCl mols/litre	Time to effect gelation secs.	Added glycocoll to a 0·3 mol/litre NaCl sol. mols/litre	Time to effect gelation secs.
0·200	13,800	0·00	230
0·200	1,460	0·05	810
0·300	225	0·10	2,700
0·325	115	0·15	6,300
0·375	28	0·20	16,200

17. Penetration in membranes.

The concept of the sieve-like membrane is due to the work of Traube in 1867 on membranes consisting of metal silicates and ferrocyanides, and of Tammann (1892) and Walden on copper ferrocyanide membranes. Series of graded membranes could be prepared, and diffusion experiments appeared to confirm the view that the permeability was governed by the pore size of the membrane and the probable volume of the hydrated ion diffusing, the hydration varying directly with the mobility and inversely with the ionic charge. Collander in 1924 established the sieve-like nature of copper ferrocyanide membranes for a series of fifty organic compounds from methyl alcohol ($V = 42{\cdot}8$) to amygdalin ($V = 467$) and found the permeability to decrease steadily with increasing molecular volume. For the acids the permeability is governed by the size of the anion; thus the series is found:

$HNO_3 >$ acetic acid $>$ sulphuric acid $>$ propionic acid $>$ citric acid.

Further support for the sieve theory is obtained from examination of the properties of collodion membranes; thus Biltz in 1910 found that dye molecules containing up to 45 atoms per molecule diffused readily, but a retardation was obtained with molecules containing 55–70 atoms per molecule, whilst beyond that permeability ceased. We have already referred to the work of Michaelis on graded collodion membranes confirming their sieve-like character. Further types of membranes for which the sieve theory has been used are membranes of compressed carbon and silica, porcelain plates graded by clogging with insoluble powders and the gelatinous ultra-filters made by Bechold and Zsigmondy, the pore size calculated with the aid of Poiseiulle's law agreeing closely with the size of the molecules whose diffusion they just prevent.

The sieve theory of permeability may, in general, be safely used when the membrane material is rigid and inert. Even if adsorption occurs the theory is still valid for those solutes which are not adsorbed (cf. Michaelis' membranes), provided that the nature and extent of adsorption remain constant factors. Thus bacterial filters, being negatively charged, adsorb basic dye cations until the surface is saturated, after which diffusion proceeds unimpeded. If an acid dye be used, there is no adsorption and no impedance. If the membrane be an ampholyte, we have seen that ionic permeability is governed by the P_{H} of the medium, but we may note that the P_{H} of the medium will likewise decide the state of swelling, i.e. the porosity of the membrane apart from the impedance caused by the electrical charge. von Risse showed that the permeability of gelatine to water was at a minimum at the isoelectric point, where the swelling is least, and increases as the P_{H} is changed in either direction away from the isoelectric point. Permeability and swelling are connected inversely to one another. In the case of collodion membranes swollen by immersion in alcohol-water mixtures a similar inverse relation between swelling and permeability to haemoglobin, water and dextrin are found. The permeability of gelatine to water and proteins is lessened by treatment with formaldehyde because such membranes are unswollen. Anselmino in 1928 has extended these observations by a comparison of the rate of diffusion of sugar and acid and basic dye-stuffs into and through gelatine, separating the two features of swelling and electric charge in this manner. Agar membranes on the other hand, which possess no marked electrocapillary properties, show similar variations of the permeability of a series of dyes with the P_{H}, but the relative speeds of diffusion of the dyes agree with the inverse order of their molecular volumes, which is a simple case of sieve action. It might be anticipated that the rate of penetration of non-electrolytes through a gelatine membrane would not be dependent only on the molecular volume, but also would be affected by the number and nature of the polar groups in the molecule. Through living cell membranes (see Hamburger and Gryns) marked lowering in speeds of penetration are obtained on insertion of polar groups in a non-polar molecule; the order of decreasing rate of penetration is found to be

$$\text{amino acid} > COOH > C{=}O > CONH_2 > OH > CHO;$$

whilst the ethyl alcohol penetrates rapidly, glycerol enters more slowly, the tetroses extremely slowly and the pentoses and hexoses not at all. A systematic investigation of the effect of polar groups on the penetration into artificial membranes in view of a possible modification of Traube's molecular volume hypothesis is evidently desirable.

Collodion membranes coated with proteins are least permeable to electrolytes at their isoelectric point, where adsorption and extension (see Ch. II) is at a maximum; the permeability according to Hitchcock increases in more alkaline and acid solutions where the adsorption is less. The permeability to water of protein-coated membranes was found to be a maximum at the isoelectric point in direct contrast to the work of von Risse and Anselmino on protein membranes. This difference in behaviour may be attributed to the blocking of the collodion pores by the swelling of the adsorbed protein. When the protein is free to expand, swelling brings an increase in porosity; but a protein layer on a rigid inert framework which cannot swell thus reverses the effect.

The factors which govern the equilibrium between disperse phase and dispersion medium will govern the amount of "free" liquid (see p. 424) available as a diffusing medium which will in turn control the permeability of the gel. Anselmino noted in gelatine that the swelling increased faster than the permeability to capillary inactive substances, which shows that the bulk of the water taken up on swelling is "bound" water; this division into bound and free water available for interfibrillar diffusion applies equally as shown by Tinker to copper ferrocyanide membranes, where the apparent pore size was found to be 15–20 $\mu\mu$ and the sieve diameter some hundred times smaller. The presence of ions or dissolved molecules which altered the proportion of free to bound water should evidently affect the permeability or apparent pore size, and may be regarded from the point of view that such addition agents effect peptisation or coagulation. Thus Bancroft and Gurchot noted the coagulation and the phenomenon of sugar permeability of ferrocyanide membranes on heating to 24° C. or on the addition of methyl alcohol, acetic acid, KCl, NaCl, $CaCl_2$. Although alkalis and water peptise the copper ferrocyanide, the impermeability to sugar of a coagulated membrane is not restored by alkalis.

It is evident that in problems of permeability* the electrocapillary data, swelling, degree of dispersion and mechanical pore size are all important factors to be considered as well as the polarity and molecular volume of the diffusing solutes. In membranes containing lipoids, especially living cell membranes, permeability was attributed by Overton (Overton u. Meyer, *Studien über Narkose*, 1904) to lipoid solubility of the diffusing material. Closely related to this hypothesis of diffusion in a homogeneous membrane is the adsorption hypothesis, which substitutes adsorption at a lipoid water interface as the criterion for permeability. If there is no intermicellar liquid present, the adsorbed solute displaces water molecules from the adsorption envelope and so penetrates.

That adsorbability from aqueous solutions should run parallel with lipoid solubility is not surprising, since both are an expression of hydrophobic character. Attempts to prepare artificial membranes of this character have been made by Thieulin, who impregnated collodion sacs with castor oil and lecithin. Such membranes are permeable to alkaloid bases but not to sodium chloride; pore size is evidently not the governing factor here. Philippson showed in the same way that impregnation with an ether extract of muscle rendered the sac impermeable to mineral salts but allowed the organic acids to pass at increasing rates in the order

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* A summarising account with references is given in Gellhorn, "Das Permeabilitätsproblem," Springer, Berlin, 1929.

$$HCOOH > CH_3COOH > CH_3OHCOOH > CH_3C_2H_5COOH.$$

Here the effect of pore size is suggested though the true relative lipoid solubility of the acids is not known. We may note that a lecithin cholesterol emulsion embedded in a dialysing thimble is stated to maintain the P_H of the internal solution constant, thus buffering is not exclusively a property of the proteins. Similar experiments by Brinkmann and Györgi have emphasised the specific nature of solution and adsorption as factors in permeability, thus the permeability of collodion to haemoglobin is increased by previous treatment with capillary active substances, e.g. sodium oleate, or with alkaloids, whereas the permeability to water is unaffected.

In none of these instances is the simple mechanism postulated by Overton entirely realised; the examination of the rate of penetration is frequently masked by the rate of storage in an intervening lipoid phase or by the slowness of a transport mechanism. This is well exemplified in the case of a gelatine gel containing methylene blue and covered with first a layer of chloroform and then one of water. Methylene blue being insoluble in chloroform is not transported from the gelatine to the water phase, but if spermaceti be dissolved in the chloroform the dye penetrates to the water, being transported by diffusion of the spermaceti micelle which in the chloroform takes up the dye. If a spermaceti soap milk be formed the chloroform layer is deeply dyed but the water scarcely coloured, for the increased solution or adsorption in the membrane material has lessened the permeability. The effect of phase inversion on the relative permeabilities of lipoid and non-lipoid materials is a factor which is probably not without biological significance.

The influence of the adsorption and ease of wetting on the penetration of liquids and solutes is well established experimentally. Thus Flusin with membranes of parchment, pig's bladder and rubber and Bartell with compressed carbon and silica membranes showed that the permeability varies with the rate of imbibition and wetting power of the solvent. Similar conclusions as to the necessity for the solvent to wet a membrane before osmosis can occur have been made by Kahlenberg. The extent of adsorption of a solute at the membrane liquid interface has been assumed by Traube to run parallel to the adsorption at an air-liquid interface. This generalisation cannot be accepted as anything more than a general guiding principle, for we have noted already, e.g. salts in water in contact with charcoal or acid and basic dyes at protein liquid interfaces, many exceptions to such a "rule."

The effect of capillary active inclusions in the membrane is well shown by the diffusion of water and organic acids through gelatine containing peptone or lecithin, examined by Traube and Dannenberg. Increasing the lipoid content of the membrane limits the amount of the water taken up correspondingly without affecting the amount of acid.

An interesting distinction between solution and adsorption has been made by Loewe for the taking up of methylene blue from aqueous solutions by various lipoids. A comparison of the calculated partition coefficients *K* and of the values of $1/n$ in an assumed Freundlich isotherm gave the following results:

Adsorbent	$\frac{1}{n}$	*K*
Cephalin ...	0·35	6·8
Cerebroside	0·16	1·64
Lipoids ...	0·22	0·51
Lanolin ...	0·15	0·012

The data support an adsorption rather than a solution mechanism. In general, however, it is hard to distinguish between adsorption and solution mechanisms, especially as most membranes are heterogeneous. The transition between adsorption in the pore of the membrane and simple solution is very gradual as the porosity of the membrane is decreased to molecular dimensions.

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